# Macromolecular Syntheses

# Board of Directors

# *Macromolecular Syntheses*

*A Periodic Publication*
*of Methods for the Preparation*
*of Macromolecules*

*VOLUME 11*
*D.A. Tirrell, Editor*

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# Submission of Preparations

Scientists are invited to submit procedures for the preparation of polymers to ***Macromolecular Syntheses***. Preparations of both old and new polymers that are of general interest or that illustrate useful preparative techniques are desired. Chemists who plan to submit preparations are urged to write to the Editor concerning their intentions.

Authors should carefully check preparations before submitting. Explicit directions should be given, including elaboration in notes where necessary, for all the steps of the preparation, isolation and characterization of the polymer. The synthesis of the starting materials or their source, along with criteria to be used in determining their purity, should be included. Experience in checking procedures for preparing polymers has shown that impure or uncharacterized starting materials present the greatest difficulty in duplicating results. The range of yields and polymer property values should be reported rather than the maximum values obtainable. Characterization of the polymer should include such information as molecular weight, viscosity, softening or melting point, elemental analysis, solubility data and especially IR and NMR spectra or spectral data. Samples of polymers may be submitted for analysis by the Editor for inclusion of spectra in the procedures.

Authors should submit three copies of their preparation to the Editor of ***Macromolecular Syntheses***:

Professor Lon J. Mathias, Editor-in-Chief
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# Dedication

To Charles G. Overberger and Herman F. Mark, two of the pioneers of modern polymer science and men who epitomize the best of scientific exploration, dedicated education, and professional integrity. Without examples such as these two provide, our personal lives would be poorer and our careers less audacious.

# Preface

Volume 11 represents a transition point in the ongoing series of polymerization procedures including ***Macromolecular Syntheses*** Volume 1-10 and Collected Volumes 1 and 2, with the last in the final stages of preparation. This monumental effort encompasses the period from inception in 1963 to the present, almost thirty years of continuous guidance and oversight by founding Editor-in-Chief, Charles G. Overberger, with the able assistance of Herman F. Mark, continuing President of the Board of Directors. The transition involves a new Editor-in-Chief and use of recently-available desk-top publishing methods to increase publication efficiency. Our goal is to maintain the standard of excellence set by these pioneers while increasing the scope and availability of the individual and collected volumes. Expansion of the scope of the series will entail:

> retyping, reprinting and reissuing Collected Volume 1;
>
> rapid publication of Collected Volume 2 using the new approach;
>
> continuing publication of individual general volumes which will then be compiled in Collected Volumes at future dates;
>
> developing focused volumes with targeted audiences, examples of such volumes currently in preparation include:
>
>> "*Living and Immortal Polymerizations and Copolymerizations," "High Performance Polymers,"* and *"Liquid Crystalline Polymers;*" each of these may include some previously-published procedures along with more recent ones to give "state-of-the-science" surveys of verified synthetic methods.

Increased availability will result from increased speed and reduced cost of printing and publication using modern computerized document and figure preparation methods. Volume 11 represents the first example of the successful implementation of this approach, and will be sold in both hard- and softcover editions. The former (at ca $35) will continue to meet the needs of libraries and individuals who require archive quality. Individual versions with softcovers will sell for $20 for professionals and $10 for students.

We welcome suggestions concerning focused volume topics and improvements in the quality and scope of this and succeeding volumes. If you find errors or mistakes, please tell us so we can correct them. With your help, we can make the continuing series of ***Macromolecular Syntheses*** an on-going tribute to its founders, and a collection of reference books of lasting value to all members of the polymer community.

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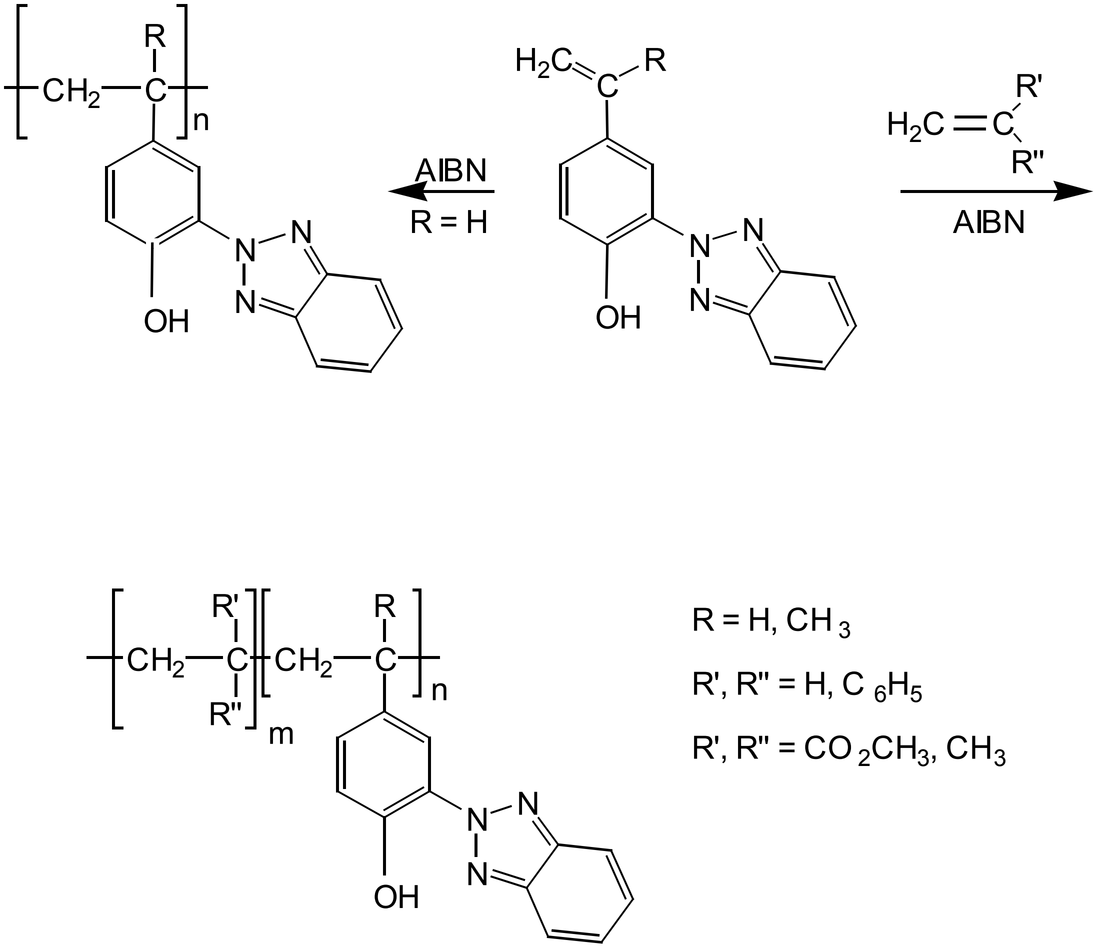
# SYNTHESIS AND POLYMERIZATION OF 2-(2-HYDROXY-5-VINYLPHENYL)-2H-BENZOTRIAZOLE AND 2-(2-HYDROXY-5-ISOPROPENYLPHENYL)-2H-BENZOTRIAZOLE

**Shanjun Li, Witold Pradellok, Zohar Nir, and Otto Vogl[1]**

Checked By: Peter Gomez and Mary Steffeck[2]



$R = H, CH_3$

$R', R'' = H, C_6H_5$

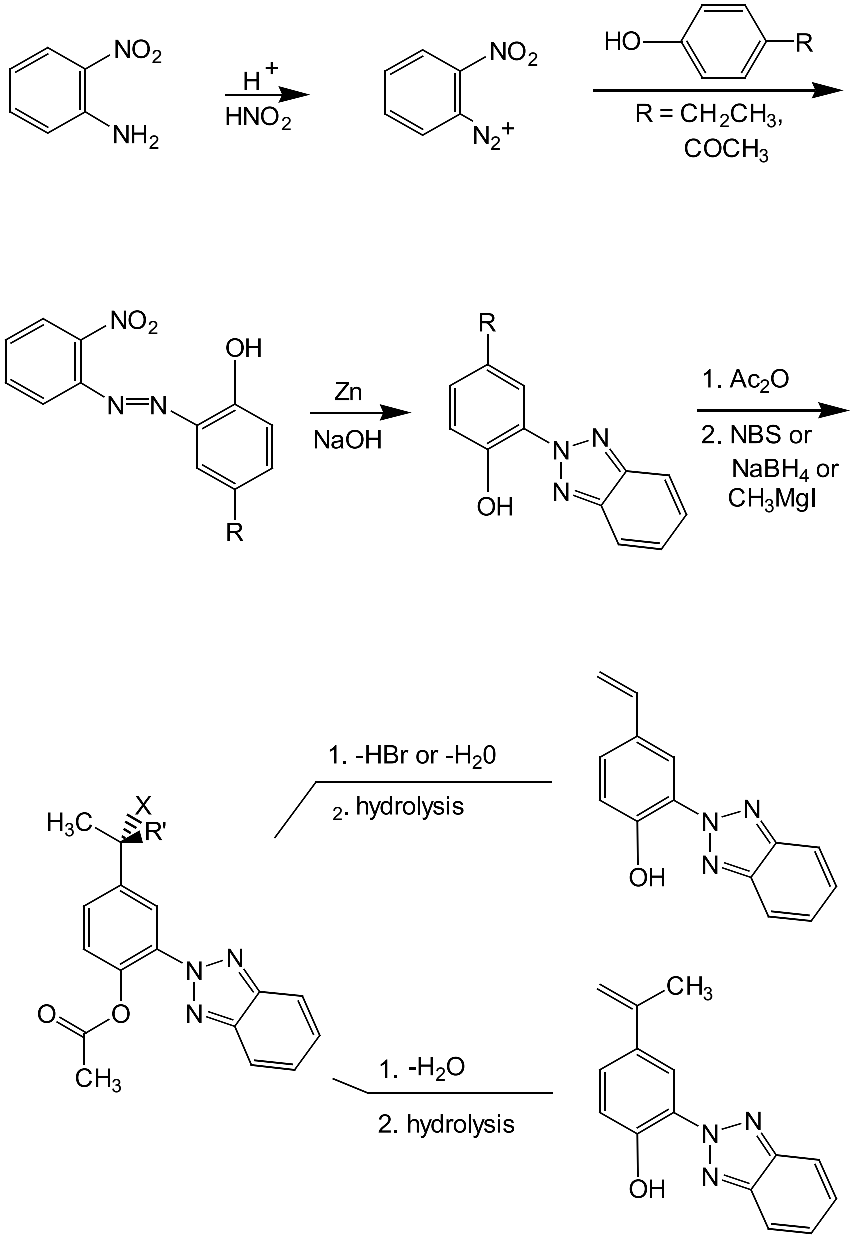
$R', R'' = CO_2CH_3, CH_3$

## 1. Procedure

### *a. Synthesis of 2-(2-Hydroxy-5-Vinylphenyl)-2H-Benzotriazole from 4-Ethylphenol* [3,4]

*2-(2-Hydroxy-5-Ethylphenyl)-2H-Benzotriazole.*

In a 2 l beaker equipped with a mechanical stirrer, a fine solid dispersion of o-nitroaniline is prepared by rapidly quenching to 0°C with vigorous stirring a warm solution of o-nitroaniline (110 g, 0.8 mol) in 300 ml of concentrated hydrochloric acid. Diazotization is carried out by dropwise addition of a solution of sodium nitrite (56 g, 0.8 ml) in water (200 ml) over a period of 1 h while the solution temperature is maintained between 0-5°C (Note 1). In the final stages of addition, the mixture became homogeneous. After the addition is complete, a small amount of insoluble material is removed by filtration while the solution is maintained near 0°C. The diazonium salt solution is added over a period of 1 h through a dropping funnel to a stirred aqueous solution (1000 ml, cooled to 15-20°C) of 4-ethylphenol (98 g, 0.8 mol), sodium hydroxide (32 g, 0.8 mol) and sodium carbonate (240 g, 2.26 mol). The azo compound separates as red oil which solidifies to a red crystalline solid (Note 2). After stirring at room temperature for 2 h, the suspension is filtered and the red solid is washed with water. After dissolving the azo compound in aqueous 2N sodium hydroxide (800 ml), the solution is placed in a cooled 2 l beaker, and zinc powder (240 g, 2.68 mol) is added in small portions over a period of 1 h to the mechanically stirred solution; a 40% aqueous solution of sodium hydroxide (250 ml) is also added over a period of 1 hour. The temperature is now raised and kept at 35-45°C for one day (Note 3); after 4 h the suspension changes color from red to green, which indicates that the azo compound has been consumed. The suspension is decanted, the residue extracted twice with 100 ml 10% aqueous sodium hydroxide, the combined solutions are cooled to 5-10°C and then acidified to pH 2 with concentrated hydrochloric acid. A dark viscous oil separates, which is extracted with chloroform (500 ml) and washed twice with water. The chloroform solution is dried with anhydrous sodium sulfate, filtered and evaporated on a rotary evaporator to give a yellow solid (135-153 g, 70-80% yield) of crude 2-(2-hydroxy-5-ethylphenyl)-2H-benzotriazole.



*2-(2-Acetoxy-5-Ethylphenyl)-2H-Benzotriazole.*

Crude 2-(2-hydroxy-5-ethylphenyl)-2H-benzotriazole (119.5 g, 0.5 mol) is acetylated for 4 h at reflux temperatures with acetic anhydride (510 g, 5 mol) and pyridine (79 g, 1 mol, Note 4). The reaction mixture is cooled to room temperature and poured into ice water (2000 ml) containing concentrated hydrochloric acid (200 ml). The mixture is extracted with a solution of chloroform (300 ml) and carbon tetrachloride (300 ml). The organic layer is washed twice with water and dried with anhydrous sodium sulfate, filtered and evaporated on a rotary evaporator. Crude 2-(2-acetoxy-5-ethylphenyl)-2H-benzotriazole is obtained in 90-95% yield (126-133 g) which is fractionally distilled through a 10 cm Vigreux column. The main fraction (185-190°C/0.075 mm) crystallizes and is further purified by recrystallization from n-heptane to give colorless needles, mp 51-52°C.

*2-(2-Acetoxy-5-[1-Bromoethyl] Phenyl)-2H-Benzotriazole.*

2-(2-Acetoxy-5-ethylphenyl)-2H-benzotriazole (126.5 g, 0.45 mol, Note 5), N-bromosuccinimide (240.3 g, 1.35 mol) in 800 ml of carbon tetrachloride are heated to reflux with 2,2'-azobis(isobutyronitrile) (1.97 g, 12 mmol, Note 6) as the catalyst, the catalyst being added in several portions over a period of 2 h (Note 7). After 5 h, the reaction mixture is filtered to remove unreacted N-bromosuccinimide and succinimide. The organic solution is washed twice each with water, 2% aqueous sodium sulfite solution, 3% aqueous sodium bicarbonate solution, and water; dried with anhydrous sodium sulfate, filtered, concentrated on a rotary evaporator and poured into methanol (1.2 l). The precipitate, crude 2-(2-acetoxy-5-[1-bromoethyl]phenyl)-2H-benzotriazole, is obtained in 80-85% yield (130-138 g). Further recrystallization from n-heptane gives pure product, mp 95-97°C.

*2-(2-Hydroxy-5-Vinylphenyl)-2H-Benzotriazole.*

2-(2-Acetoxy-5-[1-bromoethyl]phenyl)-2H-benzotriazole (36 g, 0.1 mol), acetonitrile (90 ml), tri-n-butylamine (42 ml) and picric acid (0.36 g, 1.6 mmol) are heated to reflux (Note 8). After 3 h, the reaction mixture is cooled, acidified with 6N hydrochloric acid, extracted with carbon tetrachloride, washed once with water, twice with 5% aqueous sodium bicarbonate solution, and again with water; dried with anhydrous sodium sulfate, filtered, and evaporated on a rotary evaporator. The crude 2-(2-acetoxy-5-vinylphenyl)-2H-benzotriazole (20-22 g, 70-80% yield) is then placed in the end bulb of a short path distillation apparatus (Kugelrohr), distilled at 0.075 mm and 180°C to give a yield of 11-14 g (40-50%, Notes 9 and 10). 2-(2-Acetoxy-5-vinylphenyl)-2H-benzotriazole (140 g, 0.5 mol) is dissolved in methanol (2400 ml), water (360 ml), sodium bicarbonate (100 g, 1.2 mol) and picric acid (0.23 g, 1 mmol). The mixture is heated at reflux for 1.5 h and allowed to cool to room temperature. Ice-water (600 ml) and concentrated hydrochloric acid (100 ml) is added with stirring and the product is extracted twice with chloroform (200 ml). The organic solutions are washed twice with 5% aqueous sodium bicarbonate and water, and dried with anhydrous sodium sulfate (100 g) and magnesium sulfate (80 g). After filtration and evaporation of the solution in the rotary evaporator, crude 2-(2-hydroxy-6-vinylphenyl)-2H-benzotriazole (100-113 g, 85-95% yield) is obtained. Further purification to polymerization grade monomer is accomplished by recrystallization from methanol (90% aqueous solution) to give pale yellow crystals, mp 98-99°C.

### b. Synthesis of 2-(2-Hydroxy-5-Isopropenylphenyl)-2H-Benzotriazole from 4-Acetoxyphenol [5]

*2-(2-Hydroxy-5-Acetylphenyl)-2H-Benzotriazole.*

o-Nitroaniline (55 g, 0.4 mol) is diazotized with sodium nitrite (28 g, 0.4 mol) in 150 ml concentrated hydrochloric acid and coupled with 4-acetoxyphenol (55 g, 0.4 mol) in a solution of sodium hydroxide (16 g, 0.4 mol) and sodium carbonate (120 g, 1.13 mol) in 600 ml water. The azo compound, (red crystals) is isolated, reductively cyclized with zinc powder (120 g, 1.84 mol) in 600 ml of aqueous 2N sodium hydroxide to which a 40 wt.% aqueous solution of sodium hydroxide (125 ml) is added over a period of 1 h at 35-45°C.

After one day the suspension is decanted, and the residue is extracted twice with 100 ml 10% aqueous NaOH, while keeping the temperature below 10°C, the solution is acidified to pH 2 with concentrated hydrochloric acid which precipitates a creamy solid. This is filtered and dried at 0.05 mm to give 30-35 g (30-35% yield) of crude 2-(2-hydroxy-5-acetylphenyl)-2H-benzotriazole (Note 11). Recrystallization from methanol gives white needles, mp 147-148°C.

*2-(2-Hydroxy-5-(2-Hydroxy-2-Propylphenyl)-2H-Benzotriazole.*

Dry nitrogen is passed at a constant rate into a 2 l, three-neck flask equipped with a mechanical stirrer, reflux condenser and a pressure-equalizing dropping funnel. Dry magnesium turnings (10.8 g, 0.45 mol), 200 ml of anhydrous diethyl ether, and a small amount of iodine are added and the stirring started. Methyl iodide (64 g, 0.45 mol) dissolved in anhydrous diethyl ether (50 ml) is added slowly from the dropping funnel into the stirred mixture. The reaction starts spontaneously. The methyl iodide solution is added at a rate over a period of 2 h such that the solution refluxes gently. After 2 h of addition with stirring, the Grignard reagent of methyl magnesium iodide is obtained as a grey-black solution. 2-(2-Acetoxy-5-acetylphenyl)-2H-benzotriazole is dissolved in dry tetrahydrofuran (200 ml, Note 12), diluted with diethyl ether (150 ml) and added to the Grignard reagent over a period of 30 min while keeping the solution at gentle reflux. The solution changes color. The reaction is continued for an additional 1.5 h, and is then treated with an aqueous solution of ammonium chloride (200 ml, 80 g, 1.5 mol). The organic layer is separated, the residue extracted with diethyl ether (200 ml), the combined solutions washed twice with water and dried over anhydrous sodium sulfate. The filtered solution is evaporated to give 20-24 g (50-60% yield) of pale yellow crystals which are recrystallized from diethyl ether, mp 128-129°C (Note 13).

*2-(2-Hydroxy-5-Isopropenylphenyl)-2H-Benzotriazole.*

2-(2-Hydroxy-5-(2-hydroxy--2-propenylphenyl)-2H-benzotriazole (10 g, 0.04 mol) is mixed with freshly fused potassium hydrogen sulfate (1.0 g, 10%). The mixture is placed in the end bulb of a short-path distillation apparatus (Kugelrohr) and slowly distilled at 160°C and 0.005 mm (Note 14) to give white crystals in a yield of 708 g (70-80%). Additional sublimation gives polymerization grade 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole crystals, mp 145-145.5°C (Note 15).

### c. Polymerization and Copolymerization of 2-(2-Hydroxy-5 Vinyl [or Isopropenyl] phenyl)-2H-Benzotriazole

*Homopolymerization of 2-(2-Hydroxy-5-Vinylphenyl)-2H-Benzotriazole.*

A dried 10 ml polymerization tube is charged with 2,2'-azobis(isobutyronitrile) (3.0 mg, 0.018 mmol), 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (2.0 g, 8.42 mmol) and toluene (4 ml) in this order. The homogeneous mixture is frozen in liquid nitrogen, the tube evacuated to 0.01 mm, and allowed to warm to room temperature. After repeating the freeze-thaw degassing process three times, the mixture is frozen and the tube sealed at 0.05 mm. It is then immersed in a constant temperature bath set at 50°C for 2.5 days. After cooling in an ice bath, the polymerization tube is opened, and the viscous solution is diluted with chloroform (60 ml), and filtered through a coarse glass filter. The polymer is precipitated by adding the solution slowly to 200 ml of vigorously stirring methanol. The precipitate is allowed to settle, the supernatant liquid is decanted, and the polymer is collected on a medium-porosity sintered glass funnel, redissolved in 15 ml of chloroform, and reprecipitated into methanol twice. After isolating by filtration, the polymer is washed with methanol and dried over phosphorous pentoxide at 70°C under 0.05 mm overnight to give 1.22 g (61% conversion) of white amorphous polymer with an intrinsic viscosity of 0.16 dl/g in chloroform ($C_{init}$ = 0.5 g/dl, 30°C).

*Copolymerization of 2-(2-Hydroxy-5-Vinylphenyl)-2H-Benzotriazole with Methyl Methacrylate.*

The procedure for the preparation of 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole/methyl methacrylate copolymer is very similar to the preparation of the 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole homopolymer. The polymerization tube is filled with 2,2'-azobis(isobutyronitrile) (8 mg, 0.05 mmol), 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole (0.90 g, 3.75 mmol), methyl methacrylate (2.1 g, 21 mmol) and toluene (3 ml). After polymerization at 50°C for 2.5 days, poly[2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole]-co-(methyl methacrylate) (2.8 g, 92% conversion) is obtained, with an intrinsic viscosity of 0.65 dl/g in chloroform (Note 16).

*Copolymerization of 2-(2-Hydroxy-5-Isopropenylphenyl)-2H-Benzotriazole with Styrene.*

The procedure for the copolymerization of 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole/styrene copolymer is essentially the same as for the preparation of 2-(2-Hydroxy-5-vinylphenyl)-2H-benzotriazole/methyl methacrylate copolymer. 2-(2-Hydroxy-5-isopropenylphenyl)-2H-benzotriazole (2.8 g, 11 mmol), 2,2'-azobis(isobutyronitrile) (51 mg, 0.37 mmol) and styrene (6.6 g, 63 mmol, Note 17). After the polymerization proceeds at 60°C for three days, the reaction mixture is worked up to give poly[2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole]-co-Styrene in 40% yield (3.8 g); intrinsic viscosity 0.29 dl/g in toluene (0.5 g/dl at 25°C, Note 18).

## 2. Notes

1. The diazotization of o-nitroaniline is most effectively done by preparing a very fine dispersion of the o-nitroaniline hydrochloride followed by slow addition of sodium nitrite. It is important that excess nitrous acid is destroyed with urea.
2. The azo compound deposits initially as an oil, but solidifies upon cooling in good yield (>90%).
3. Although a number of reagents have been recommended for the reduction of o-nitroazo compounds including sodium dithionite, the reduction with zinc powder in aqueous sodium hydroxide is the standard reducing agent for the reductive cyclization of o-nitroazo compounds to benzotriazoles. Completeness of the reduction to the benzotriazole ring usually requires higher temperature or longer reduction times at the end of the reaction.
4. The acetylation is also done with sulfuric acid as catalyst, but the yield is normally lower than with pyridine.
5. For the bromination with N-bromosuccinimide, the use of pure 2-(2-acetoxy-5-ethylphenyl)-2H-benzotriazole is best. Distilled but not recrystallized material can also be used.
6. Since 2,2'-azobis(isobutyronitrile) is used at the boiling point of carbon tetrachloride (76°C), it has a relatively short half-life of about 80 min, consequently repeated addition of smaller portions is necessary.
7. The reaction is easily followed by $^1$H NMR measurement of the reaction mixture after periodic withdrawals of samples.
8. Dehydrobromination of substituted 1-bromoethyl benzene derivatives is the key step for the procedure to introduce vinyl groups. Various techniques for the dehydrobromination of 1-bromoethyl compounds of acetylphenols have been studied. One method consists of the use of a mixture of a tertiary amine (tri-n-butylamine) as the base in N,N-dimethylacetamide solution at about 145°C; the other method uses triethylamine in refluxing acetonitrile solution. The rate of dehydrobromination in acetonitrile is faster than in N,N-dimethylacetamide.
9. Short-path (Kugelrohr) distillations rather than regular fractional distillation should be carried out in order to avoid or minimize polymerization of the vinyl compound formed during the distillation since deacetylation occurs to some extent.
10. 2-(2-Hydroxy-5-vinylphenyl)-2H-benzotriazole is also prepared from 4-acetoxyphenol. 2-(2-Acetoxy-5-acetylphenyl)-2H-benzotriazole is reduced to 2-(2-acetoxy-5-[1-hydroxyethyl]phenyl)-2H-benzotriazole with sodium borohydride in diethyl ether solution, then dehydrated by distillation with potassium hydrogen sulfate in the presence of picric acid. After hydrolysis and acidification, crude 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole is obtained as pale yellow crystals in 60% yield (based on 2-(2-acetoxy-5-acetylphenyl)-2H-benzotriazole).
11. Commonly the yield of the reaction is 30-35%, although yields as high as 50% were obtained.
12. 2-(2-Acetoxy-5-acetylphenyl)-2H-benzotriazole is not very soluble in diethyl ether. Therefore, tetrahydrofuran is used as the solvent, while diethyl ether is used as the solvent for the Grignard reagent.
13. In the course of the workup and isolation of the carbinol from the Grignard reaction, the acetoxy group is also hydrolyzed to give 2-(2-hydroxy-5-[2-hydroxy-2-propylphenyl])-2H-benzotriazole. Purification is not crucial as this crude product can be directly dehydrated.
14. No stabilizer (radical scavenger) is needed for the distillation of 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole.
15. 2-(2-Hydroxy-5-isopropenylphenyl)-2H-benzotriazole can also be recrystallized from n-hexane or methanol.
16. The copolymerization procedure described here can also be used for the copolymerization of 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole with styrene or n-butyl acrylate.
17. The copolymerization of 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole with styrene is most conveniently carried out in bulk.
18. All attempts to homopolymerize 2-(2-hydroxy-5-isopropenylphenyl)-2H-benzotriazole in toluene with 2,2'-azobis(isobutyronitrile) as the initiator were unsuccessful.

## 3. References

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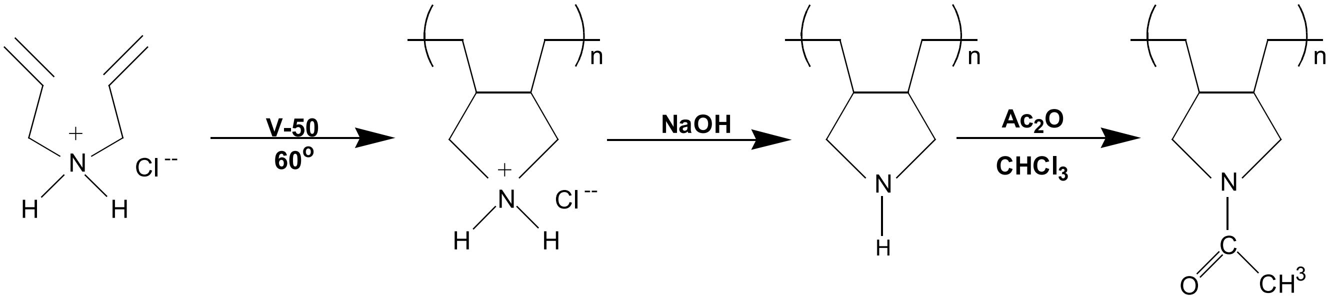
# POLY(3,4-DIMETHYLENE-N-ACETYLPYRROLIDINE)

## Lon J. Mathias, Rajeev A. Vaidya and Terry B. Parsons[1]

Checked by: George B. Butler and Jen-Chi Chen[2]



### 1. Procedure

*a. Poly(3,4-dimethylenepyrrolidine)*

A portion of freshly distilled diallylamine (5.0 g, 0.0515 mol, Note 1) is dissolved in 6.18 g (10% excess) of concentrated hydrochloric acid (36% aqueous solution). The temperature is maintained close to 0°C throughout the dissolution process. The solution is degassed (Note 2) and transferred to a 30 ml jacketed reactor. Initiator (0.14g, 1 mol-% of V-50)[3] is added to the stirred solution (Note 3). The reactor head-space is purged with nitrogen for 10 min. The nitrogen flow rate is then reduced to a minimum and fluid from a controlled temperature bath held at 60°C is circulated through the jacket (Note 4). Polymerization is continued with constant stirring under a nitrogen atmosphere for 24 h.

The highly viscous solution obtained is diluted with an equal portion of deionized water to reduce the viscosity to a manageable level. The diluted solution is cooled in an ice bath and twice the stoichiometric amount of 6N sodium hydroxide is slowly added to the stirring solution. The precipitated polymer (a tacky gel) is separated from the supernatant solution by filtration or decantation. The polymer is then washed with deionized water and lyophilized (Note 5). The polymerization has been carried out on small (5 ml) to large (250 ml) quantities of diallylamine with variable results. Conversions were usually in the range of 50-75%, although occasionally a polymerization did not go at all.

*b. Poly(3,4-methylene-N-acetylpyrrolidine)*

Finely divided poly(3,4-methylenepyrrolidine) (2.0 g, 0.0206 mol) is dissolved in 30 ml of reagent grade chloroform. The polymer takes 4-5 h to dissolve and gives a cloudy solution that appears to be on the brink of phase separation. Acetic anhydride (6.31 g, 0.0618 mol) is added to the solution and the mixture allowed to react at room temperature for 24 h. The resulting polymer solution has a clear, light yellow color with no cloudiness. The polymer is precipitated by adding the reaction mixture to 300 ml of cold dry ether. The gelatinous precipitate is separated by decantation and washed with more dry ether. Finally, the polymer is dried under vacuum for 24 h to give 2.4 g of product (40% conversion, Note 6).

### 2. Characterization

The free polyamine is insoluble in most common organic solvents and forms cloudy solutions in chloroform. The structure is confirmed by IR and $^{13}C$ spectra of solutions of the polymer in aqueous hydrochloric acid (Note 7, Spectra 1 and 2).

The acetylated polymer is very soluble in chloroform and gives an intrinsic viscosity of 0.5 dl/g (Note 8). The structure is confirmed by IR (thin film) and $^{13}C$ (chloroform) spectra of the polymer (Note 9, Spectra 3 and 4).

## 3. Notes

1. Commercial diallylamine (Aldrich Chemical Company) is 98% pure and is straw yellow in color. After vacuum distillation (60-65°C at 38 mm Hg), the monomer is colorless.
2. The flask containing the solution is evacuated while in the ice bath and the contents held under vacuum for 10 min.
3. *t*-Butylhydroperoxide (Lucidol, 90% aqueous solution) and a $TiCl_3/H_2O_2$ redox system[4] have been used as initiators for the cyclopolymerization of diallylamine. However, V-50 gives cleaner, higher molecular weight polymer and faster rates of polymerization.[3]
4. A simple water or oil bath held at approximately 60°C may also be used.
5. Freeze drying is not necessary but gives an easily handled dry sample of polymer. Vacuum drying may also be used but usually results in the polymer collecting on the walls of the flask as a tough film. The checkers dialyzed their sample (Spectrum wet tubing with MW cut-off of 1000) and obtained a yield of 3.72 g (74% conversion).
6. Most of the acetic acid (by product of the acetylation) is removed from the polymer during the precipitation and washing steps. Acetic acid may be reduced to trace levels by repeating these steps. The checkers obtained 2.24 g (30% conversion) of acetylated polymer.
7. The IR spectrum is obtained in aqueous HCl using a Barnes Analytical Circle Cell[3] and a Nicolet 5DX FTIR. The $^{13}C$ NMR spectrum is obtained in aqueous HCl with a JEOL FX90Q ($CH_3OH$ external reference).
8. Viscosities are measured at 30°C using a Cannon-Ubbelohde #50 viscometer. The checkers obtained an intrinsic viscosity of 0.32 dl/g.
9. The IR spectrum is obtained on a thin film cast from chloroform. The $^{13}C$ NMR spectrum is obtained on a 30% chloroform solution.

## 4. Methods of Preparation

Diallylamine hydrochloride was one of the first monomers to be cyclopolymerized.[6,7] The original polymerization was carried out using t-butylhydroperoxide, a very slow initiator, at 65°C for four days. The N-benzoyl derivative of the polyamine was prepared under Schotten-Baumann conditions.[7] Copolymerization of diallylamine with diallylacetamide in aqueous HCl using ammonium persulfate as the initiator has been patented,[8] but no information on yield or copolymer composition was reported.

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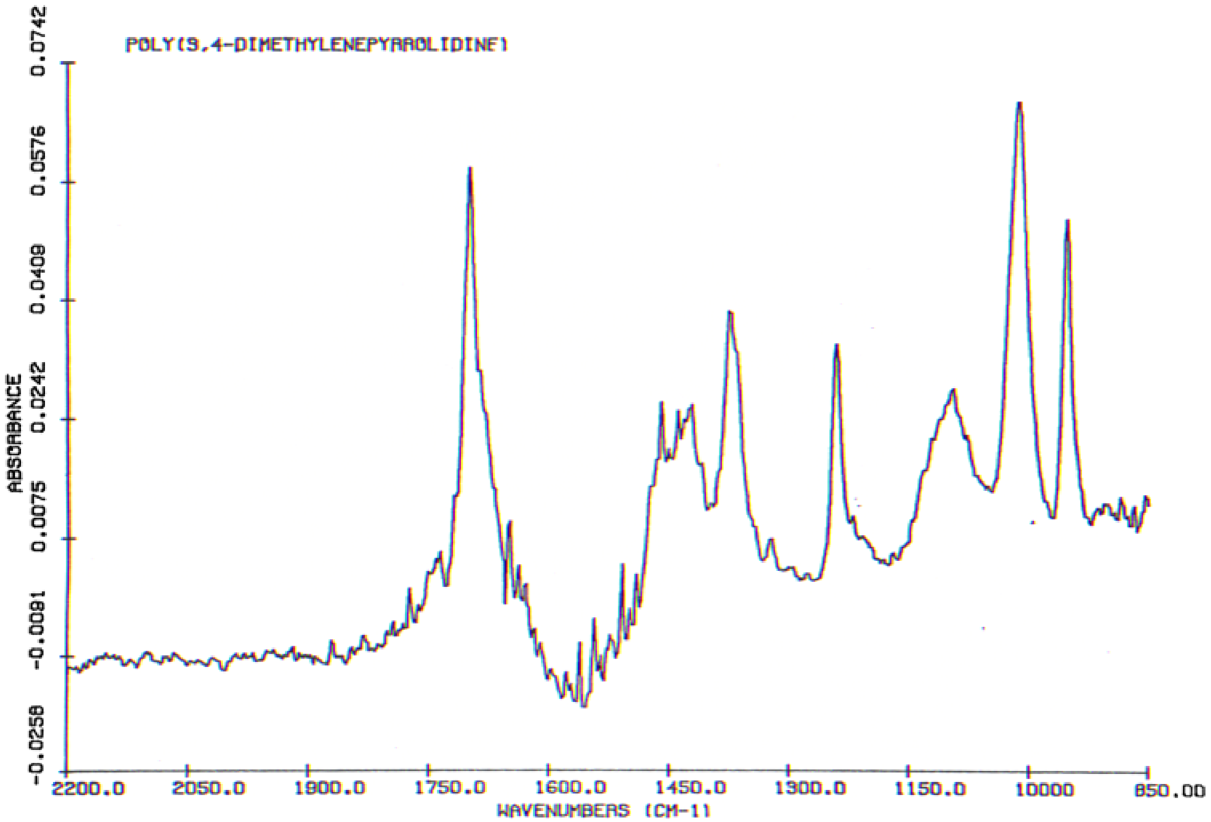
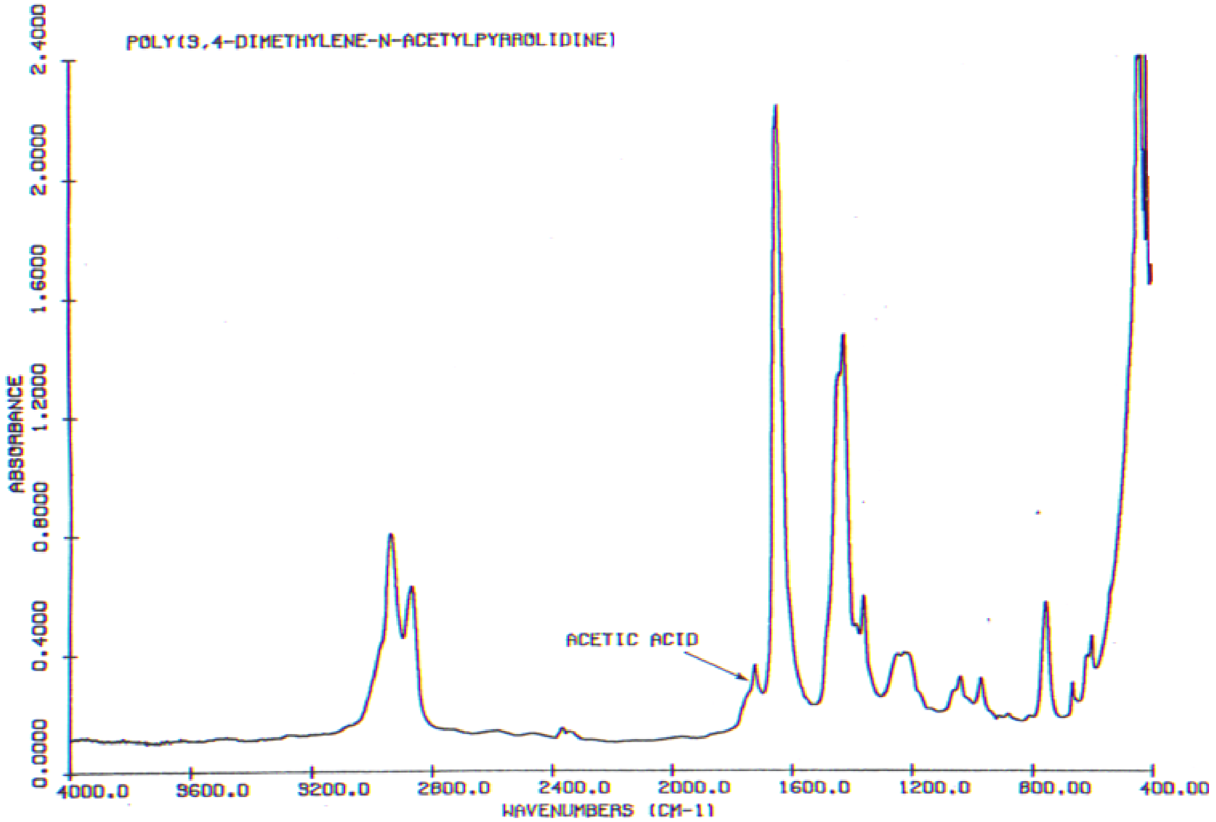
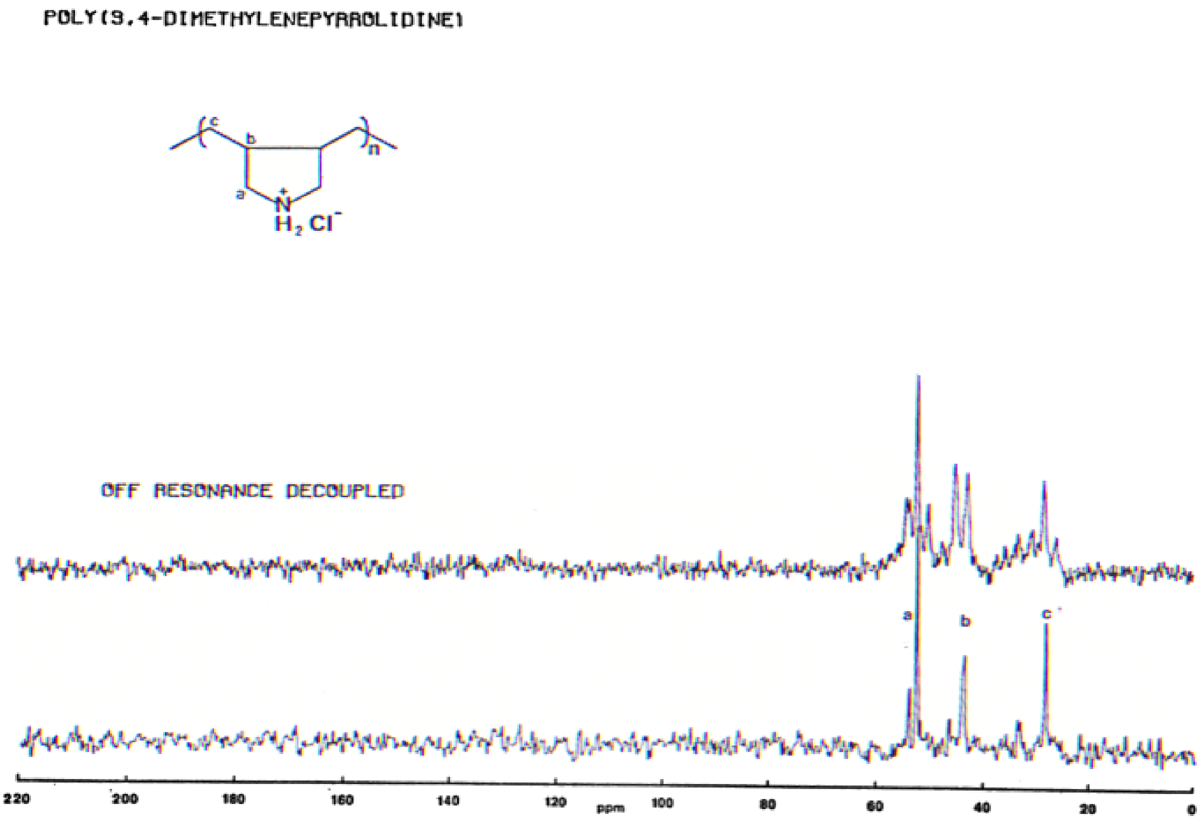


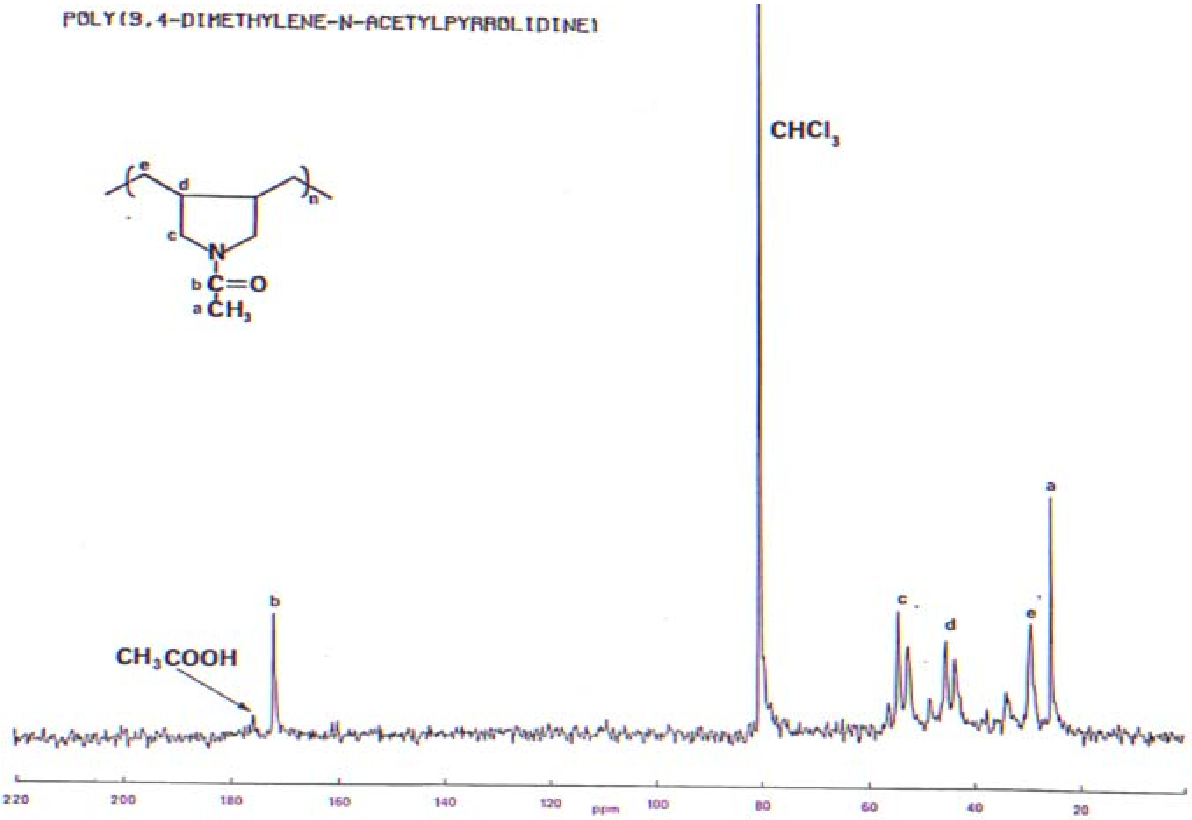
Spectrum 1. FT-IR of poly(3,4-methylenepyrrolidine) in aqueous HCl.



Spectrum 2. FT-IR of a think film of poly(3,4-methylene-N-acetyl-pyrrolidine) cast from chlorine.



Spectrum 3. 13C NMR of poly(3,4-methelenepyrrolidine) in aqueous HCl.

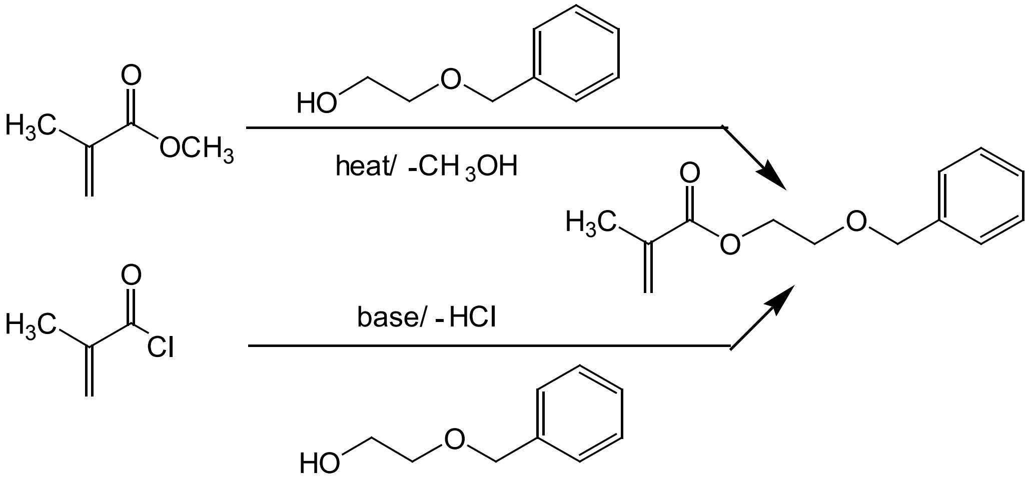


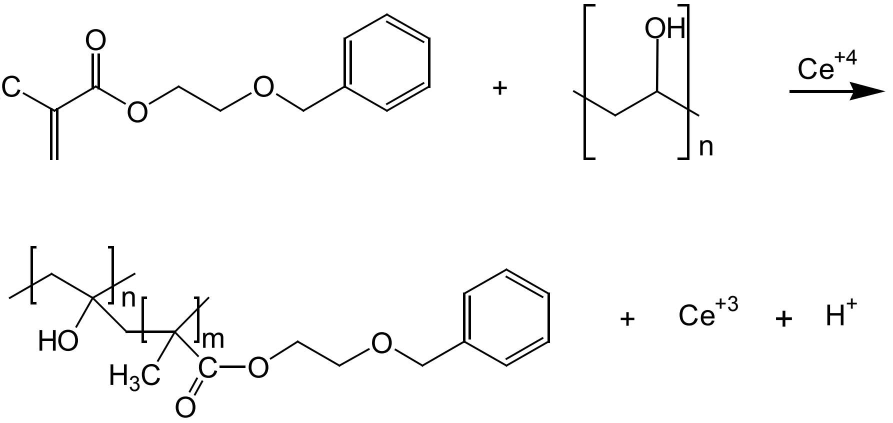
Spectrum 4. $^{13}C$ NMR of poly(3,4-methylene-N-acrtylpyrrolidine) in $CHCl_3$.

# GRAFT COPOLYMER OF POLY(VINYL ALCOHOL) AND 2-BENZYLOXYETHYL METHACRYLATE

**Ruth Silberman**[1]

Checked by: B. Johnson, S. Mahaphasukwat and C.L. McCormick[2]





## 1. Procedure

*a. Monomer Synthesis: (BzOEMA)*

*Procedure A:* [3] A 250 ml round-bottomed flask is equipped with a soxhlet extractor and a reflux condenser. In the flask are placed methyl methacrylate (65 g, 0.65 mol), 2-benzyloxyethanol (76.0 g, 0.5 mol, Note 1), 2 g of p-toluenesulfonic acid, and a small amount of catechol (Note 2). The extraction thimble is filled with 54 g of activated molecular sieves type 13A (Note 3). The reaction mixture is refluxed for 8 h, during which traces of catechol are added. After cooling, the organic phase is washed with water, dried over anhydrous sodium sulphate and fractionally distilled in the presence of p-benzoquinone. The esterification product is extracted with n-hexane to remove the product from any residual 2-benzyloxyethanol. The hexane extract is washed with water and dried over anhydrous sodium sulphate. After distilling off the n-hexane, the product is collected at 125°C/0.8 mm Hg.

*Procedure B:* [4,5] An alternative procedure is favored to prepare the monomer. **Caution! This synthesis should be carried out in a well-ventilated hood. Gaseous HCl and methacryloyl chloride are noxious materials.** A mixture of 2-benzyloxyethanol (41 g, 0.27 mol) and a trace of p-benzoquinone (Note 4) is placed in a three-neck flask. The flask is immersed in an ice-water bath and equipped with a stirrer, a thermometer, a dropping funnel and a reflux condenser. Methacryloyl chloride (27 g, 0.26 mol) is added dropwise over 45 min. The ice-water bath is then removed and stirring is continued for another hour, until no more hydrogen chloride is evolved. The reaction mixture is washed with water, then with an aqueous solution of sodium bicarbonate and then with water again. The organic phase is dried over anhydrous calcium sulphate. The product is distilled under reduced pressure through a Vigreux column in the presence of p-benzoquinone. The esterification product is collected at 83°C/0.1 mm Hg. The yield of 2-benzyloxyethyl methacrylate is 33.75 g (59%, Note 5).

*b. Polymerization:* [6] *(Note 6)*

The graft polymerization reaction is carried out in a temperature-controlled bath fitted with a shaking device. Poly(vinyl alcohol) (1.0 g, MW 72,000, degree of hydrolysis 99%) is dissolved in 100 ml of dimethyl sulfoxide. 2-Benzyloxyethyl methacrylate (4.0 ml, density 1.06 g/ml) and 2.5 ml of the ceric ammonium nitrate initiator solution (Note 7) are added to the solution.[7] The reaction mixture is heated to 30°C for 3 h under an argon atmosphere. The graft copolymer is precipitated into acetone, filtered or centrifuged, washed with water and dried under reduced pressure at 35°C. The yield of the graft polymer PVA-g-BzOEMA is 2.56 g (48%).

*c. Characterization:*

*Solubility:* The graft polymer is insoluble in most organic solvents, but is highly soluble in dimethyl sulfoxide and moderately soluble in dimethyl formamide, pyridine, methyl pyrrolidone and formic acid.

*Viscosity measurements:* The intrinsic viscosity measured in dimethyl sulfoxide at 30°C with an Ubbelhode viscometer is 0.42 dl/g (Note 8).

*Grafting efficiency:* The grafting efficiency is determined from the following equations:

$$\%\ \text{grafting} = 100\ \text{x}\ \frac{\text{Total wt. of PVA-g-BzOEMA} - \text{Wt. of PVA}}{\text{Total wt. of PVA-g-BzOEMA}}$$

$$\%\ \text{conv} = 100\ \text{x}\ \frac{\text{Total wt. of PVA-g-BzOEMA} - \text{Wt. of PVA}}{\text{Wt. of BzOEMA}}$$

A series of graft copolymers with various compositions were synthesized (Note 9). For the above-described composition, the percent of grafting was 61% and the percent conversion was 41%.

*Spectral Analysis:* The principal IR assignments are as follows (in cm$^{-1}$): 3650 (OH), 1710 (C=O), 1600 (aromatic C-C), 1040 (C-O-C). The $^1$H NMR analysis gave a poorly-resolved spectrum. However, it showed a broad multiplet at 7.25, which was assigned to the aromatic protons.

## 2. Notes

1. 2-benzyloxyethanol is prepared according to Butler, et al.[8] It distills at 90°C/0.3 mm Hg; purity is verified by gas chromatography and $^1$H NMR spectroscopy.
2. Catechol is used as an inhibitor of polymerization.
3. Molecular Sieves type 13A are absorbants for methanol. They are activated by heating (metal bath, 250°C, 5 h) under reduced pressure.
4. p-benzoquinone is used to inhibit polymerization.
5. Direct esterification gives increased yields over transesterification although both give identical characteristics for the 2-benzyloxyethyl methacrylate:
   HR-MS (m$^+$/z): 220.115; IR (cm$^{-1}$): 1720 ( " ,$-unsaturated ester), 1640 (C = C), 1600 (aromatic ring).
   $^1$H-NMR [* from $(CH_3)_4Si$]: 6.9 (5H, aromatic); 5.6 and 5.00 (1H each, $CH_2$ = C); 4.0 (2H, N$CH_2$); 3.8 and 3.2 (2H each, O-$CH_2$-$CH_2$); 1.5 (3H, $CH_3$).
6. Homopolymerization of the monomer 2-benzyloxyethyl methacrylate is conducted with 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator.

7. The initiator, 0.1 M $Ce^{+4}$ in 1.0 M nitric acid, is prepared by recrystallization of ceric ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$ from 70% nitric acid by precipitating the salt through addition of ammonium nitrate.[7]
8. Viscosity measurements were determined for various compositions of the graft copolymer. Viscosity decreases with an increase in initiator concentration and reaction time. Increased reaction temperature up to 40°C lowers viscosity, but at higher temperatures the viscosity increases. This is due to oxidation of the hydroxyl group on PVA.[8]
9. Percent grafting and conversion increase with initiator concentration, reaction time and reactant concentration.[9] Increased acetyl content of PVA decreases the extent of grafting and conversion. Increased monomer concentration increases percent grafting but decreases percent conversion. Elevated reaction temperature increases percent grafting and conversion up to 40°C; at higher temperatures these decrease significantly.

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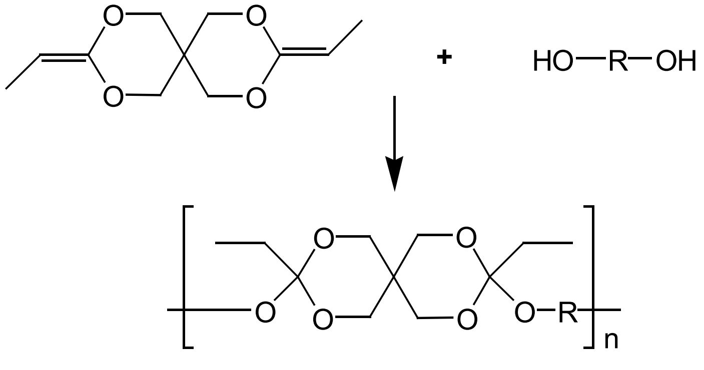
# POLY(ORTHOESTERS) BY THE ADDITION OF DIOLS TO A DIKETENE ACETAL

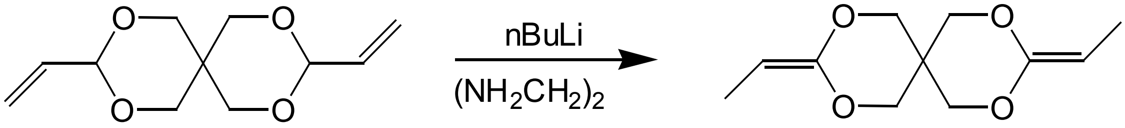
**S.Y. Ng, D.W.H. Penhald and J. Heller[1]**

Checked by: G. Zhang and D.A. Tirrell[2]



## 1. Procedure

*a. Preparation of 3,9-bis(ethylidene-2,4,8,10-tetraoxaspiro[5,5]undecane)*



In a 3 l three-necked flask fitted with a mechanical stirrer, argon inlet tube, thermometer and rubber septum is placed 1.2 l of ethylene diamine (Note 1). The flask is cooled with ice water and the contents kept at about 8°C (Note 2) under an argon atmosphere. A hexane solution of n-butyllithium (130 g, 2 mol, Note 3) is added via a stainless steel hypodermic U-tube pushed through the rubber septum using carefully controlled argon pressure over a period of 1 h. Next, a mixture of 3,9-bis(vinyl-2,4,8,10-tetraoxaspiro[5,5]undecane) (530 g, 2.5 mol, Note 4) and 0.5 l of ethylenediamine is cooled to 8°C and added to the three necked flask (Note 5). After stirring at 8°C for 3 h, the reaction mixture is poured into 3 l of ice-water with vigorous stirring. The aqueous mixture is extracted twice with 1 l portions of hexane. The combined hexane extracts are washed three times with 1 l portions of water, dried over anhydrous magnesium sulfate and filtered under suction. The filtrate is evaporated to dryness on a rotary evaporator to give crude material (413 g, 78%) containing 90% of 3,9-bis(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane) (Note 6).

The crude product is dissolved in 2 l of hexane containing 10 ml of triethylamine (Note 7) and the solution placed in a 4 l filter flask, sealed and stored in a freezer at -20°C for two days (Note 8). The crystals thus formed are collected by basket centrifugation (Note 9) at -5°C under an argon atmosphere. Distillation of the brownish product (Note 10) through a 12 in vigreaux column at reduced pressure gives 3,9-bis-(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane)(313 g, 61%, Note 11) as a colorless liquid, b.p. 82°C (0.1 torr) which crystallizes at room temperature, mp 30°C; characteristic IR band at 1700 cm$^{-1}$.

*b. Preparation of Polymer*

While maintaining anhydrous conditions, *trans*-cyclohexanedimethanol (89.57 g, 0.621 mol), 1,6-hexanediol (39.52 g, 0.334 mol) and 1.8 l of tetrahydrofuran distilled over calcium hydride are placed into a 5 l three necked flask equipped with an overhead stirrer, an argon inlet tube and a condenser on a trap (Note 12). The mixture is stirred until all solids have dissolved; then 3,9-bis(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane) (206.75 g, 0.974 mol) is added. The polymerization is initiated by the addition of 0.5 ml of a 20 mg/ml solution of *p*-toluenesulfonic acid in tetrahydrofuran (Note 13).

The polymerization temperature rapidly rises to the boiling point of tetrahydrofuran and then gradually decreases. Stirring is continued for about 2 h, then 1 ml of triethylamine stabilizer is added and the reaction mixture very slowly poured with vigorous stirring into about 5 gallons of methanol containing 10 ml of triethylamine.

The precipitated polymer is collected by vacuum filtration and dried in a vacuum oven at 60°C for 24 h to give 325 g (98.8% yd). Typical molecular weights are 50,000 to 100,000 as determined by light scattering.[3] The molecular weight can be controlled by skewing the reaction stoichiometry.[4]

*c. Methods of Preparation*

Although the superbase-catalyzed rearrangement of allyl ethers to propenyl ethers has been reported,[5,6,7] we are not aware of any work that describes the rearrangement of vinyl acetals to ketene acetals. We have found that this rearrangement proceeds readily and is thus an excellent alternative method for the synthesis of ketene acetals which are usually prepared by the dealcoholization of ortho esters.[8]

Poly(ortho esters) were first reported in a series of patents by the Alza Corporation and were prepared by a transesterification reaction between diethoxytetrahydrofuran and diols.[9,10,11,12] Another family of poly(ortho esters) also prepared by a transesterification reaction has recently been reported.[13] However, unlike both of these syntheses, which require long reaction times, the addition of alcohols to ketene acetals proceeds to completion virtually instantaneously.[14] Furthermore, because no small molecule by-products are produced, dense, crosslinked matrices can be produced by using varying proportions of diols and triols.[15]

## 2. Notes

1. Commercial ethylenediamine is used as received.
2. Ethylenediamine freezes at 5°C.
3. Hexane solutions of n-butyllithium of any practical concentration can be used.
4. 3,9-bis(vinyl-2,4,8,10-tetraoxaspiro[5,5]undecane) from Aldrich is purified by flash distillation with a short distillation head at 120°C and 0.5 torr. This compound can be prepared by reacting pentaerythritol with 20% excess of acrolein and catalytic amounts of acid using benzene as a drying solvent.[14]
5. The mixture can be added rapidly to the three-necked flask but the cooling capacity of the ice-bath must be adequate so that the reaction temperature does not rise above 8°C.
6. Analysis is conducted by GC on a 30 meter capillary column at an initial temperature of 40°C increasing to 225°C at a rate of 20°C/min.
7. Triethylamine is used as a stabilizer since 3,9-bis(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane) is extremely unstable under acidic conditions. However, it is stable under basic conditions.
8. Seeding may be necessary.
9. Pressure filtration can be used but filtration under suction is not satisfactory.
10. Distillation removes high boiling and colored by-products.
11. One crystallization usually gives a product 98% pure. Because a purity better than 99% is required, a second crystallization is necessary.
12. All reagents must be handled under anhydrous conditions and should be at least 99% pure.
13. The polymerization is exothermic. A condenser on a trap to prevent the reaction mixture from boiling over should be used.

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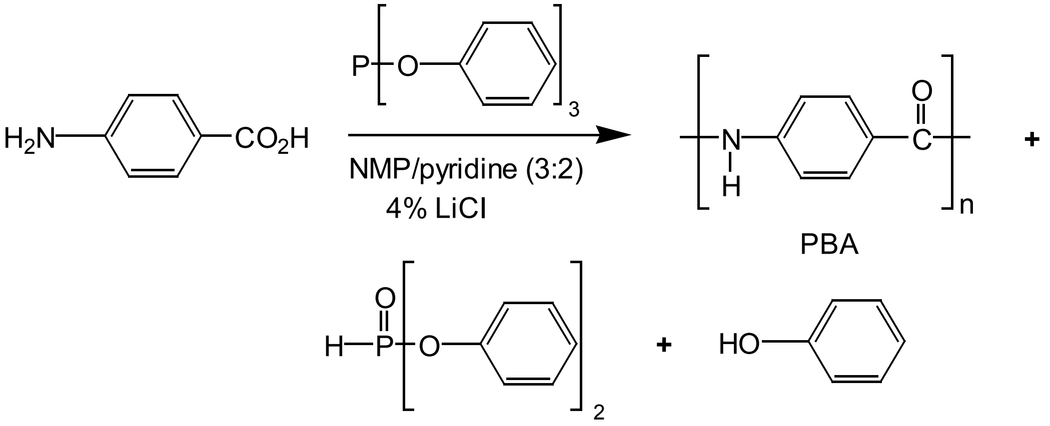
# POLY(P-BENZAMIDE) OF MODERATE MOLECULAR WEIGHT BY YAMAZAKI PHOSPHORYLATION REACTION

**J. Preston[1], R. Kotek[2], and W.R. Krigbaum[3]**

Checked by: S.J. Grossman and S.F. Wang[4]



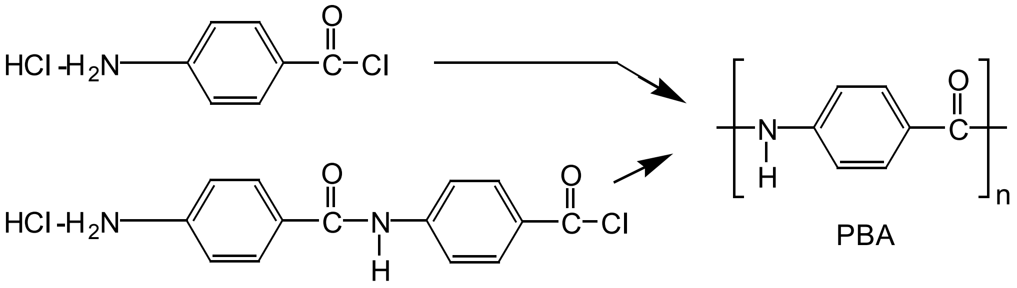
This type of reaction was first described by Yamazaki, et al,[5] and the reaction conditions were modified by Preston and Hofferbert.[6]

## 1. Procedure

A dry 250 ml three-neck conical flask is placed in a constant temperature oil bath (Note 1). The flask is fitted with a condenser, mechanical stirrer (Note 2) and an inlet and outlet for nitrogen gas. To remove air and traces of moisture, the flask is flushed with a stream of nitrogen dried by passing through a 20 cm column of Fisher G-16 mesh S-160 silica gel. To this prepared vessel are added *p*-aminobenzoic acid (2.743 g, 0.02 mole), 20 ml of N-methyl-2-pyrrolidone (NMP) containing 4% LiCl, 20 ml of pyridine, and triphenylphosphite (5.25 ml, 0.02 mol, Note 3). The oil bath is heated to 100°C, and this temperature is maintained for 3 hours. Poly(*p*-benzamide), PBA, is isolated by pouring the very viscous solution into rapidly stirring methanol in a blender jar. The polymer is washed in the blender with three 200 ml portions of methanol, and refluxed with 200 ml of methanol for 1 hour. After drying in a vacuum oven at 60°C to constant weight, the yield of polymer is nearly quantitative. The inherent viscosity of the polymer is 1.7 ± 0.2 dl/g (Note 4). PBA does not melt below 500°C. Polymer having inherent viscosity 1.5 to 1.6 dl/g forms a nematic phase at a concentration of 10.7 g/dl in dimethylacetamide containing 3% LiCl (Note 5).

## 2. Methods of Preparation

Poly(*p*-benzamide), PBA, of high molecular weight ($0_{inh}$ \$ 3.5 dl/g) can be prepared by the use of acid chloride monomers:[7,8]



PBA of higher molecular weight ($0_{inh}$ = 2.4 to 3.0 dl/g) can be obtained by using reaction conditions similar to those described here, but employing as monomer 4,N-(4N-aminobenzamido)benzoic acid.[9,10]

## 3. Notes

1. The Techne TE-7/P oil bath, which maintains the temperature within ± 0.5°C, is very suitable. The polycondensation can also be performed in a boiling water bath as described by Preston and Hofferbert.[6]
2. An ACE Trubore stirring shaft, bearing and Teflon stirrer blade turned on-end permit good stirring of the reacting solution.
3. Freshly distilled liquids must be used for best results. NMP (Aldrich or Eastman) is stored over Type 4A molecular sieves (Fisher Scientific) and distilled from $CaH_2$ under reduced pressure. Pyridine is stored over BaO and distilled from NaOH pellets. Triphenylphosphite is purified by vacuum distillation. Dried *p*-aminobenzoic acid from Aldrich (mp 188-189°C) is pure enough to be used as received. LiCl is dried at 180°C for 24 hours.
4. The inherent viscosity is measured at 25°C using a 0.1% solution in 96% $H_2SO_4$, with a Cannon-Ubbelohde viscometer having a solvent flow time of at least 150 seconds. The checkers obtained poly(*p*-benzamide) of inherent viscosity 1.3 dl/g.
5. Additional information about the lyotropic behavior of this polymer can be found in the literature.[11]

## 4. References

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# POLY(*P*-PHENYLENETEREPHTALAMIDE) OF HIGH MOLECULAR WEIGHT BY THE HIGASHI PHOSPHORYLATION REACTION

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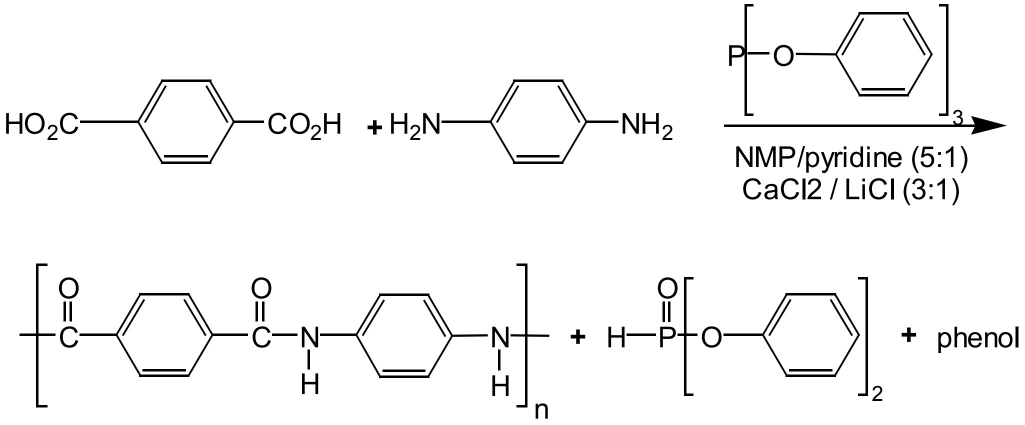
Checked by: S.J. Grossman and S.F. Wang[4]



These reaction conditions were first reported by Higashi, Ogata and Aoki.[5]

## 1. Procedure

Into a constant temperature oil bath (Note 1) is placed a dry three-neck conical flask fitted with a condenser, mechanical stirrer (Note 2) and an inlet and outlet for nitrogen gas. To remove air and traces of moisture, the flask is flushed with nitrogen which is dried by passing it through a 20 cm column of Fisher 6-16 mesh S-160 silica gel. To the prepared vessel are added terephthalic acid (0.831 g, 0.005 mol) , *p*-phenylenediamine (0.541 g, 0.005 mol), a LiCl/$CaCl_2$ solution in pyridine/N-methyl-2-pyrrolidone (NMP) (Note 3) and triphenylphosphite (2.65 ml, 0.01 mol, Note 4). The oil bath is heated to 100°C and this reaction temperature is maintained for 3 h. The gel is removed using a spatula and ground in a blender jar containing methanol. The poly(*p*-phenyleneterephthalamide), PPD-T, is washed three times in the blender with 200 ml of methanol and refluxed with 200 ml of methanol for 1 h. After drying in a vacuum oven at 60°C to constant weight, the polymer yield is nearly quantitative. The inherent viscosity determined is 4.2 to 4.5 dl/g. PPD-T does not melt below 500°C.

## 2. Methods of Preparation

Poly(*p*-phenyleneterephthalamide) of high molecular weight can be prepared[6,7] by the reaction of terephthaloyl chloride with *p*-phenylenediamine in nonprotonic amide solvents, and this route is used commercially for the preparation of PPD-T.

PPD-T of somewhat higher molecular weight, $0_{inh}$ up to 6.2 dl/g, has been prepared[8] using conditions similar to those reported here.

## 3. Notes

1. The Techne TE-7/P oil bath is suitable for this experiment. It allows temperature control to within ± 0.5°C.
2. An ACE Trubore tubing shaft, bearing a Teflon stirrer blade turned on-end, is used to give good stirring of the reaction mixture.
3. To a dried Erlenmeyer flask having a ground glass stopper are added 50 ml NMP, 1 g LiCl, 3 g $CaCl_2$ and 10 ml of pyridine. This mixture is stirred with a magnetic stirring bar for 30 to 50 minutes to produce a slightly cloudy solution which is used in the polycondensation reaction.
4. For best results, the liquids used in the polycondensation reaction should be freshly distilled. NMP (Aldrich or Eastman) is stored over type 4A grade 513 molecular sieves (Fisher Scientific) and distilled from $CaH_2$ under reduced pressure. Pyridine is stored over BaO and distilled from NaOH pellets.

Purification of triphenylphosphite (Aldrich or Eastman) is performed by vacuum distillation. Terephthalic acid (Amoco) is of fiber grade purity and *p*-phenylenediamine is obtained from Fisher Scientific. LiCl and $CaCl_2$ can be dried at 180°C for 48 h.

5. The inherent viscosity was measured using a Cannon-Ubbelohde viscometer at 25°C using a 0.1% solution in 96% $H_2SO_4$.

## 4. Merits of the Preparation

The procedure given here is suitable for the preparation of all AA-BB aromatic polyamides, including those with all *para*-linkages, all *meta*-linkages, and mixed *meta*- and *para*-linkages.

## 5. References

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3. Department of Chemistry, Duke University, Durham, NC 27706.
4. Department of Plastics Engineering, University of Lowell, Lowell, MA 01854.
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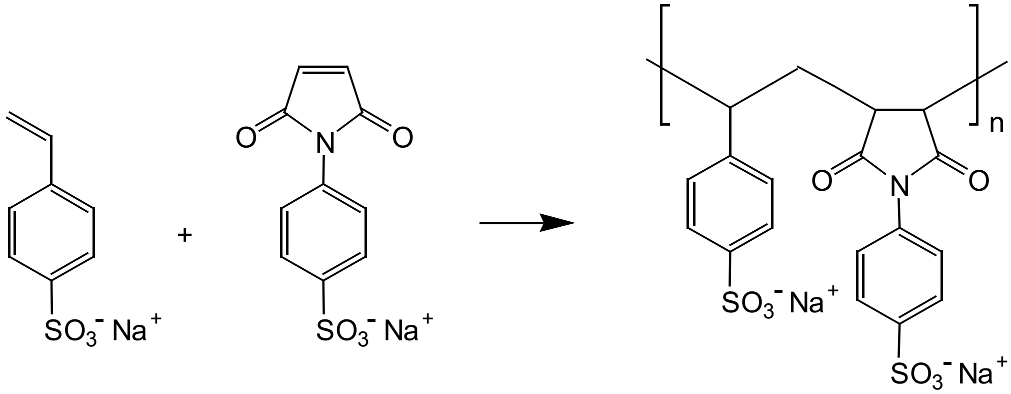
# POLY(SODIUMSTYRENESULFONATE-ALT-SODIUMN-(4-SULFOPHENYL MALEIMIDE)

**S. R. Turner[1], W.A. Thaler[2], and R. Wardle[3]**

Checked by: J.C. Salamone and R.E. Richard[3]



## 1. Procedure

To a stirred solution of sodium N-(4-sulfophenyl)maleimide (10.0 g, 36.4 mmol, Note 1) and sodium styrenesulfonate (7.49 g, 36.4 mmol, Note 2) in 10 ml of deoxygenated water at 50°C under positive nitrogen pressure is added 0.010 g of potassium persulfate. This solution is kept at the 50°C reaction temperature for 24 h. The polymer is isolated by adding the polymerization solution slowly to 2000 ml of stirring acetone. The pinkish fibrous precipitate thus obtained is filtered and dried under vacuum to give 14.28 g (81.6% yield).

## 2. Notes

1. Sodium N-(4-sulfophenyl)maleimide is prepared in two steps as follows:
a) N-(4-sulfophenyl)maleamic acid - A solution of maleic anhydride (35.0 g, 357 mmol) in 250 ml of absolute methanol is added to a stirred solution of sulfanilic acid sodium salt monohydrate (54.0 g, 234 mmol) in 1000 ml of absolute methanol. After the solution is stirred for less than 5 min at room temperature, a yellow precipitate forms. The reaction is allowed to continue for 20 min and then the precipitate is filtered and dried under vacuum to yield 67.8 g (99.1%).
b) Sodium N-(4-sulfonyl)maleimide - A slurry of sodium acetate (0.8 g, 9.8 mmol) and the maleamic acid from above (16.0 g, 54.6 mmol) in 200 ml of acetic anhydride is refluxed until a color change to a tannish solution is noted. The solution is cooled to room temperature and diluted with 200 ml of a 3:2 mixture of absolute ethanol and acetone. The mixture is filtered and the precipitate slurried again in 200 ml of the 3:2 ethanol:acetone solution. Filtration and vacuum drying yields 10.23 g (68.1%) of the maleimide monomer suitable for polymerization (Note 3).
2. Sodium styrenesulfonate was purchased from Air Products and Chemicals, Inc., Allentown, PA 18105, and was used as received. Potassium p-styrenesulfonate (used by the checkers) obtained from Polysciences, Inc., Warrington, PA 18976 may also be used.
3. Previous preparations of this maleimide monomer involved cyclization of the maleamic acid in N,N-dimethylaniline[4] (which proved difficult to remove), or with large amounts of sodium acetate in acetic anhydride,[5] i.e., up to 50% by weight based on the maleamic acid. This excess sodium acetate is found difficult, if not impossible, to remove from the water soluble maleimide monomer. The conditions reported here involve an order of magnitude less sodium acetate. At this level it is easily separated from the monomer, and thus monomer of sufficient purity for polymerization studies is readily obtained.

## 3. Characterization

Nitrogen and sulfur elemental analyses for the 1:1 alternating copolymer are calculated to be: N, 2.92%; S, 13.36% and found to be: N, 3.05%; S, 13.57%. (The checkers obtained the following elemental analysis which corresponds to the dihydrate of the copolymer containing potassium p-styrenesulfonate: calculated N, 2.64%; S, 12.01%; found N, 2.68%; S, 11.98%.) This same composition is obtained over a broad comonomer feed ratio, thus substantiating the alternating nature of the copolymerization.[6] The infrared spectrum shows the characteristic carbonyl and sulfonate bands. It is identical to that of a polymer sample prepared by modifying an existing styrene-maleic anhydride alternating copolymer first with sulfur trioxide to sulfonate the aromatic group and then with the sodium salt of sulfanilic acid to convert the anhydride unit to the imide.[6]

Reduced viscosity versus concentration plots in distilled water at 25°C show typical strong polyelectrolyte behavior. An intrinsic viscosity of approximately 2.0 is measured in 2% sodium chloride solution at 25°C.

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# PHOTOCROSSLINKABLE POLYMERS WITH PENDANT IMINO SULFONATE GROUPS

## M. Shirai, M. Tsunooka, and M. Tanaka[1]

Checked by: S.J. Keipert[2]

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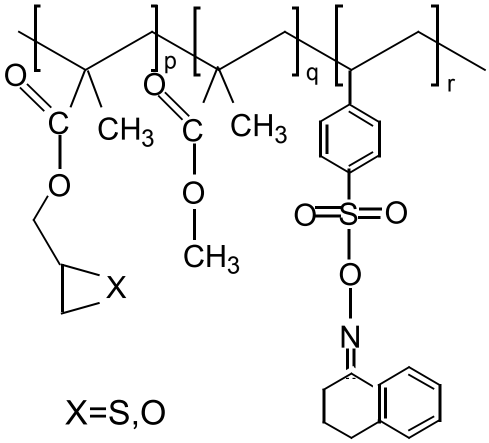


## 1. Procedure

*a. 1,2,3,4-Tetrahydronaphthylideneimino p-styrenesulfonate (**I**):*

To a solution of tetralone oxime (13.7 g, 0.085 mol, Note 1) in 32 ml pyridine cooled below 10°C is slowly added *p*-styrenesulfonyl chloride (19 g, 0.094 mol, Note 2). With vigorous stirring the reaction is continued below 20°C for 3 h. The reaction mixture is poured into 360 ml of ice-cold 5% aqueous HCl and extracted with chloroform. After washing the chloroform layer with water thoroughly, the chloroform layer is dried with $K_2CO_3$ and evaporated under reduced pressure. The oily residue is continuously extracted with hot *n*-heptane, which yields white crystals upon cooling. Recrystallization from *n*-heptane gives pure product (6.4 g, 23%); mp 80-82°C. (Notes 3 and 4).

*b. Copolymerization of **I** and 2,3-epoxypropyl methacrylate:*

A pyrex glass tube with stopcock is charged with **I** (0.2 g), 2,3-epoxypropyl methacrylate (10 ml, Note 5), 2,2'-azobis(isobutyronitrile) (AIBN, 0.025 g, Note 6), and THF (10 ml) are degassed under vacuum by repeated freeze-thaw cycles. The solution is cooled to 15°C and irradiated with a high-pressure mercury lamp (Note 7) for 4 h. The reaction mixture is poured into an excess of ethyl ether and the precipitate filtered. The polymer is then purified by dissolving in tetrahydrofuran (THF) and precipitating with ethyl ether (Note 8). The yield of copolymer is 30% (Note 9).

*c. Ternary polymerization of **I**, 2,3-epithiopropyl methacrylate, and methyl methacrylate:*

**I** (0.15 g), 2,3-epithiopropyl methacrylate (2.96 g, Note 10), methyl methacrylate (7.5 ml, Note 11), AIBN (0.031 g, Note 6), and benzene (10 ml) are placed in a pyrex glass tube with stopcock. The solution is degassed under vacuum by repeated freeze-thaw cycles, cooled to 15°C, and irradiated with a high-pressure mercury lamp (Note 7) for 3 h. The reaction mixture is poured into an excess of ethyl ether and the precipitated polymer is purified by dissolving in THF and precipitating into ethyl ether (Note 8); yd 9.2% (Note 12).

## 2. Characterization

The copolymer and the ternary polymer are soluble in common organic solvents such as benzene, dichloromethane, chloroform, and THF, and they have good film-forming properties. The films of polymers show $8_{max}$ at 254 nm and a very weak shoulder around 300 nm. The molecular weights of polymers are determined by GPC using a polystyrene standard and THF as solvent; the results are shown in the Table along with the contents of **I** in polymers as determined by measuring UV absorbance at 254 nm in $CH_2Cl_2$ (Note 13). The ratio of methyl methacrylate units to 2,3-epithiopropyl methacrylate units of the ternary polymer is determined from the proton intensity ratio, "-$CH_3$ (*=0.9)/-O-$CH_3$ (*=3.6), of the $^1$H NMR spectrum of the polymer in $CDCl_3$.

TABLE. Copolymer molecular weights and compositions.

| | | | | Composition in mole % | | |
|---|---|---|---|---|---|---|
| | X | Mn x $10^{-4}$ | Mw/Mn | p | q | r |
| Copolymer | O | 3.9-6.7 | 1.9-2.2 | 98-99 | 0 | 1-2 |
| Ternary polymer | S | 5.6-9.8 | 1.7-1.9 | 25-27 | 72-75 | ca 1 |

## 3. Photocrosslinking of Polymers

The copolymer and the ternary polymer are photocrosslinkable (Note 14). The efficiency of photocrosslinking of the ternary polymer is slightly higher than that of copolymer (Note 15). The insoluble fraction of the irradiated films increases with increases in the post-irradiation heating time in the dark, although no insolubilization is observed on heating the films without irradiation (Note 16). The efficiency of photocrosslinking of the ternary polymer is slightly higher than that of poly(2,3-epoxypropyl methacrylate) and the copolymer of 2,3-epithiopropyl methacrylate and methyl methacrylate (30:70), both of which contain the same amount of 1,2,3,4-tetrahydro-1-naphthylideneimino *p*-toluenesulfonate.[3]

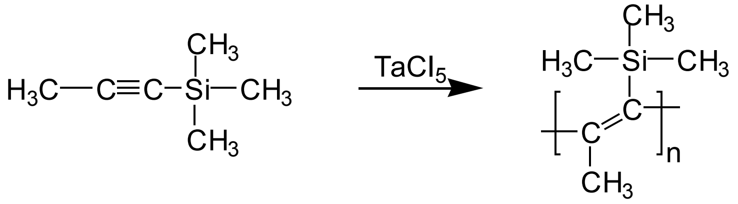
## 4. Notes

1. Tetralone oxime is conveniently prepared. 1-Tetralone (45 g, 0.31 mol), hydroxylamine hydrochloride (34.2 g, 0.50 mol), ethanol (112 ml), and water (22 ml) are placed in a four-necked round bottomed flask equipped with mechanical stirrer and a thermometer. To the reaction mixture is added powdered NaOH (61.2 g, 1.53 mol) portionwise. Efficient cooling is necessary. After addition, the reaction mixture is refluxed for 10 min, cooled to room temperature, and poured into 1300 ml of 5% aqueous HCl. The precipitate is separated by filtration and recrystallized from water-methanol (1/6 V/V) to give 28.9-35.4 g (58-71%); mp 102-104°C (lit. mp 100-102°C[4]).
2. *p*-Styrenesulfonyl chloride is conveniently prepared according to the method reported by Iwakura, et al.[5] Potassium *p*-styrenesulfonate (50 g, 0.23 mol, available from Polysciences, Inc.), *p*-hydroquinone (0.5 g), and 300 ml of chloroform are placed in a round-bottomed flask fitted with mechanical stirrer and a thermometer. The mixture is cooled to 10°C and with vigorous stirring, $PCl_5$ (60 g, 0.29 mol) is added portionwise over a period of 1 h at 10°C. The reaction is then continued at 45-50°C for 3 h, cooled and filtered. The filtrate is evaporated until no chloroform can be detected. The oily residue is extracted with ethyl ether and washed with cold water several times. The ether layer is dried with $CaCl_2$ and evaporated until no ether can be detected. The product is used without further purification; yd 19.0-26.6 g (41-59%).
3. Spectral data of **I** are as follows: IR(KBr): 1370 and 1180 $cm^{-1}$ (O-S-O); $^1$H NMR ($CDCl_3$): 8.00-7.15 (m, 8); 6.00-5.30 (m, 2); 2.95-2.65 (m, 4); 2.05-1.75 ppm (m, 2). Elemental analysis: calcd. for $C_{18}H_{17}NO_3S$: C, 66.06%; H, 5.19%; N, 4.28%. Found C, 66.27%; H, 5.39%; N, 3.85%.
4. The checkers recommend an alternative work-up. Emulsions that may form in the course of the extractive work-up with chloroform and water may be broken with brine. Rather than using a continuous extraction, the checkers added four 50 ml portions of hot heptane to the oily product. A yield of 5.3 g (19%) was obtained. After crystallization from 500 ml of hot heptane, the melting point of the product was 83-86°C.
5. A reagent grade of 2,3-epoxypropyl methacrylate (Wako Pure Chemical Co., Ltd.) is distilled under reduced pressure before use.
6. 2,2'-Azobis(isobutyronitrile) (AIBN, Wako Pure Chemical Co., Ltd.) is recrystallized from ethanol.
7. A high-pressure mercury lamp (Toshiba SHL-100 UV, 75 W) is employed with a glass filter (Toshiba UV-35) to cut off wavelengths shorter than 350 nm. The checkers used a 400 Watt medium pressure

# POLY[ 1-(TRIMETHYLSILYL)-1-PROPYNE]

## Toshio Masuda[1]

Checked by: Brian Hilker and Bernard Gordon[2]



## 1. Procedure

The polymerization procedure is carried out under dry nitrogen (Note 1). A 100-ml flask equipped with a three-way stopcock is flushed with dry nitrogen, and charged with 1-(trimethylsilyl)-1-propyne (55 mmol, 6.1 g, 8.3 ml, Note 2) and toluene (19 ml, Note 3) via hypodermic syringes. This monomer solution is maintained at 80$^{o}$C. Tantalum pentachloride ($TaCl_5$, 1.0 mmol, 360 mg, Note 4) is placed in another 100-ml flask equipped with a three-way stopcock, the flask is flushed with dry nitrogen, toluene (25 ml) is added with a syringe, and the metal chloride is completely dissolved by keeping the flask at 80$^{o}$C for 15 min. Then 25 ml of the monomer solution is added with a syringe to the catalyst solution. Polymerization is continued at 80$^{o}$C for 3 h (Note 5).

Polymerization is terminated by adding a 1:9 v/v solution (25 ml) of methanol and toluene to the stirring reaction mixture. The polymer formed is dissolved in toluene (2 l) with stirring. The solution is poured little by little into methanol (20 l) under stirring. The precipitated polymer is allowed to stand overnight, filtered off, washed with methanol, and dried to a constant weight (Note 6). The polymer yield is 5.5 g (100%, Note 7).

## 2. Characterization

The weight- and number-average molecular weights ($M_w$ and $M_n$) of the polymer are 7.3 x $10^5$ and 1.3 x $10^5$, respectively, according to gel permeation chromatography (Note 8). The intrinsic viscosity in toluene at 30$^{o}$C is 5.43 dl/g.

*Elemental Analysis:* Calcd. for $(C_6H_{12}Si)_n$: C, 64.20%; H, 10.78%. Found: C, 64.11%; H, 10.97%. The salient features of the IR spectrum (KBr pellet) are peaks at 2950 (m), 2850 (m), 1540 (m), 1240 (s), and 820 (s) cm$^{-1}$. The $^1$H NMR spectrum ($CDCl_3$ solution) shows rather broad peaks at * 1.7 and 0.1 ppm. The $^{13}$C NMR spectrum ($CDCl_3$ solution) is characterized by peaks at * 151, 140, 25 and 1 ppm. The x-ray diffraction analysis indicates that this polymer is amorphous.

Poly[1-(trimethylsilyl)-1-propyne] is a white or beige-tinged solid. The UV-visible spectrum in cyclohexane shows only a very small absorption in the UV region (8$_{max}$ 273 nm, ,$_{max}$ 120 l · mol$^{-1}$ · cm$^{-1}$), and none above 340 nm.

The polymer is soluble in toluene, xylene, cyclohexane, hexane, $CCl_4$, $CHCl_3$ and THF, but insoluble in 1,2-dichloroethane, anisole, diethyl ether, ethyl acetate, acetone, aniline, nitrobenzene, N,N-dimethylformamide and dimethyl sulfoxide. Casting a toluene solution of the polymer gives a tough transparent film.

The polymer softening point is 345$^{o}$C. This polymer shows no molecular weight change nor oxidization even when heated in air at 100$^{o}$C for 20 h. Weight loss does not occur below 300$^{o}$C based on thermogravimetric analysis in air.

Tensile properties of the polymer are as follows: Young's modulus 630 MPa, tensile strength 40 MPa, elongation at break 73%. The glass transition temperature is above 200$^{o}$C according to the dynamic mechanical measurement.

## 3. Notes

1. Since the active species for the polymerization is sensitive to moisture, oxygen and polar impurities, it is essential to remove these from the reaction system. All glassware is oven-dried overnight at 130°C. Liquid reagents are manipulated with hypodermic syringes.
2. 1-(Trimethylsilyl)-1-propyne can be obtained from Farchan Laboratories, Inc. (USA) or from Petrarach Systems, Inc. (USA). This monomer is distilled from calcium hydride (bp 100°C/760 torr).
3. Toluene as polymerization solvent is washed with 5% sulfuric acid, water, 10% sodium hydroxide solution and water, dried over calcium chloride overnight, distilled twice from calcium hydride, and stored over Linde 3A molecular sieves under dry nitrogen.
4. $TaCl_5$ (purity >99%) is commercially available (e.g. from Alfa or Morton Thiokol, Inc., USA), and can be used without further purification. It is convenient to store $TaCl_5$ in many small sealed ampoules and use one ampoule each time. Since $TaCl_5$ is sensitive to moisture but rather stable to air, it can be weighed out in dry air without decomposition, if the weighing is done quickly.
5. The catalyst solution is yellow. As the polymerization proceeds, the system turns brown and solidifies. When the reaction is terminated with a methanol-toluene mixture, the system becomes virtually white.
6. The polymer is air-dried for a few days, and then vacuum-dried for a few more days.
7. Since the decomposed catalyst is mostly soluble in methanol, the amount of catalyst residue in the polymer is negligible (<0.3 wt%). However, if it is necessary to remove the catalyst residue as completely as possible, the polymer is dissolved in toluene and reprecipitated into a large amount of methanol.
8. Gel permeation chromatograms were obtained on a Jasco Triroter liquid chromatograph using Shodex A802, A804, A806 polystyrene gel columns with $CHCl_3$ as eluent. $M_w$ and $M_n$ were estimated based on polystyrene calibration.

## 4. Discussion

The title polymer can be obtained only by use of Ta catalysts (such as $TaCl_5$) and Nb analogs.[3,4] If a 1:1 mixture of $TaCl_5$ and $Ph_3Bi$ is employed as catalyst, a polymer whose $M_w$ reaches 4 x $10^6$ forms quantitatively.[5] The present polymer is characterized by its high oxygen permeability.[3,6] Various homologues of poly[1-(trimethylsilyl)1-propyne] have also been prepared.[7,8]

## 5. References

1. Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
2. Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802.
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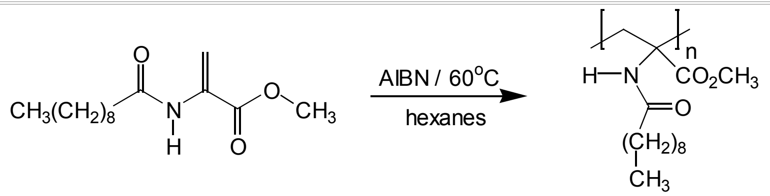
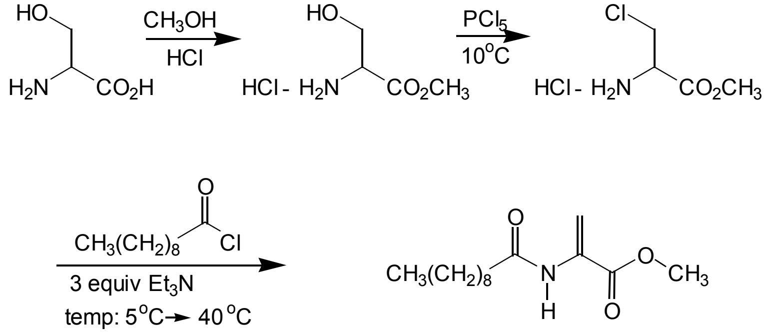
# POLY(N-DECANOYLDEDEHYDROALANINE METHYL ESTER) [POLY(METHYL-2-DECANAMIDOPROPENOATE)]

## L.J. Mathias and R.E. Hermes[1]

Checked by: C.G. Overberger, R. Bloodworth and A. Tsuei[2]





## 1. Procedure

*a. Monomer Synthesis*

**Caution! These operations should be carried out in a well-ventilated hood. Benzene and 2-nitropropane are cancer-suspect agents.** Decanoyl chloride and $PCl_5$ are noxious materials. A 500 ml round bottom flask is charged with 3-chloroalanine methyl ester-HCl (8.70 g, 50 mmol, Note 1) and 200 ml hexene, and equipped with a magnetic stirbar and serum stopper. The suspension is stirred in an ice bath while triethylamine (7.0 ml, 50 mmol) is added using an oven-dried syringe. After 15 min, small portions of triethylamine (7.0 ml total volume) and decanoyl chloride (10.5 ml, 50 mmol) are added alternately over 1 h. The reaction temperature is held below 10°C for an additional hour before slowly adding a final equivalent of triethylamine (7.0 ml) to effect the dehydrohalogenation step. The stirred suspension is placed in a 40°C water bath for 2 h, and then refrigerated overnight. The cold suspension is filtered through a coarse fritted-glass funnel to remove the triethylamine-HCl salt. The filtrate is washed twice (500 ml separatory funnel) with 50 ml portions of 0.1N HCl and twice with 50 ml water. The light yellow organic layer is rotary evaporated below 40°C to obtain a yellow oil; crude yield 97% (Note 2). A white crystalline product is obtained from mixed hexanes at -15°C; mp 10.3-11.5°C (Note 3). The checkers suggest that flash chromatography is an effective method of purification for this monomer as well (Note 4).

*b. Polymerization*

An oven-dried test tube is charged with monomer (1.0 g, 4 mmol), 6 ml hexanes, and 2,2′-azobis(isobutyronitrile) (AIBN) initiator (5-50 mg). The tube is closed with a septum and purged with dry nitrogen for 5 min before suspending it in a 60°C oil bath. Gelation occurs within 4 h although the polymerization is continued for up to 20 h. Some solvent is usually lost by evaporation/diffusion through the septum. The clear polymer gel is dissolved in 5 ml tetrahydrofuran and precipitated into stirring ice-cold methanol (10-fold excess). The polymer mass is removed with forceps and oven dried at 70-80°C overnight; yd >65%.

## 2. Characterization

The FTIR spectra of monomer and polymer are shown in Figure 1. The vinyl absorption at 1635 cm$^{-1}$ is clearly visible in the monomer while it is absent in the polymer. The C=0 stretch of both the methyl ester and amide functional groups are evident in both spectra (monomer: 1726, 1692 cm$^{-1}$, polymer: 1739, 1682 cm$^{-1}$) along with the amide II band at 1515 cm$^{-1}$.

The $^{13}$C NMR spectra are compared in Figure 2. Peak assignments are based on calculated chemical shifts and comparison to model compounds. Monomer vinyl peaks at 130.5 and 109.1 ppm have clearly been converted to polymer backbone carbons observed at 43.0 and 62.0 ppm, respectively. The polymer sample was analyzed by NMR at 80$^{o}$C to sharpen the backbone and carbonyl carbon peaks, and was found to be essentially atactic by high resolution $^{13}$C NMR.

The polymer side-chain crystallinity is shown by both WAXS and DSC. The DSC trace displays a slight endotherm at 70$^{o}$C (side-chain melting) with a backbone melting endotherm at 190$^{o}$C.

Polymers have been obtained with molecular weights ranging from 100,000 to 3.6 million.[3] Dilute solution viscosity measurements were made in THF at 25$^{o}$C using a #50 Cannon-Ubbelohde viscometer. Light scattering (LALLS) data was obtained using a Chromatix KMX-6 spectrophotometer. The Mark-Houwink relationship between intrinsic viscosity [0] (dl/g) and weight-average molecular weight $M_w$ is given below.

$$[0] = 2.63 \text{ x } 10^{-4} M_w^{0.63}$$

The polymer is soluble in many organic solvents such as chloroform, methylene chloride and benzene, but only swells in petroleum ether, acetic acid, DMAc, DMF, and methanol. The polymer is insoluble in acetonitrile, DMSO, water, and ethanol.

## 3. Notes

1. Methyl 2-amino-3-chloropropanoate-HCl or 3-chloroalanine methyl ester-HCl[3] is prepared from commercial D,L-serine methyl ester-HCl. A 1 l reaction kettle is equipped with a mechanical stirrer and charged with 300 ml 2-nitropropane and phosphorous pentachloride (230 g, 1.1 mol). The suspension is stirred in an ice bath while D,L-serine methyl ester-HCl powder (155.6 g, 1.0 mol) is added in small portions over a period of 2 h. The mixture is left at ice temperature overnight. The semi-solid mass is filtered through a fritted glass funnel under nitrogen purge. The white crystalline product is recrystallized from hot absolute methanol, filtered, and rinsed with methylene chloride, and then acetone. The fine white crystalline product is vacuum dried and stored in a refrigerated desiccator; yield >76%; mp 137.9-138.3$^{o}$C (lit.[4] mp 134-136$^{o}$C). Chloroform, carbon tetrachloride and methylene chloride have also been used as reaction solvents but were found to give unpredictable yields and a mixture of products.
2. The method described here has been used as a general preparation of alkylamidodehydroalanine methyl esters with carbon chain lengths of 2-18.[5]
3. The purified monomer is very reactive in the liquid state, and care should be taken to reduce time spent at room temperature. We observed one sample spontaneously polymerize to very high molecular weight ([0] = 8.8 dl/g, $M_w$ = ca 15 million) at ca 0$^{o}$C.
4. Crude monomer (150 mg) is isolated by flash chromatography on silica gel (50 x 130 mm column, 10:1 hexane/ethyl acetate, 40 ml fractions) to afford 75 mg of pure monomer as a colorless oil; TLC $R_f$ = 0.19 (10:1 hexane/ethyl acetate). The purified monomer can be stored under nitrogen for more than one week at 0-5$^{o}$C.

## 4. Method of Preparation

Dehydroalanine (Dha), the vinyl analogue of alanine (Ala), is a component of many naturally occurring peptides which exhibit antibiotic properties. These antibacterial polypeptides have been isolated from numerous sources and contain as many as eight dehydroalanine residues. This fact, coupled with the search for new synthetic antibiotics, generated much interest in the preparation of peptides containing biologically active dehydroalanine residues. A review of dehydroamino acids, including dehydroalanine-containing peptides, appeared in 1979.[6]

Many synthetic methods have been established for the introduction of the dehydroalanine residue into peptides. Indirect routes include base-catalyzed elimination reactions on substituted residues of *N*-hydroxy-,[7] *N*_chloro-,[8] and 3-chloroalanine;[9,10,11] ester elimination from 2-acetoxyamino acids,[12] and tosyl esters of serine (Ser)[13] and threonine;[14] and Hofmann elimination from 2,3-diamino acids.[15] Other methods have recently been reported and include direct elimination from cysteine using silver carbonate[16] and the dehydration of serine residues using isoureas,[17] carbodiimides,[18] and a triphenylphosphine-azidodicarboxylate complex.[19] Simpler analogs have been prepared by the direct condensation of pyruvic acid with various amides to produce N-substituted derivatives of dehydroalanine.[20,21] In fact, *N*-acetyldehydroalanine [2-acetamidoacrylic acid] is currently available commercially.[22]

Synthetic polymers have been prepared from various *N*-substituted derivatives of dehydroalanine and are the subject of numerous patents and publications. British (1946)[21] and US (1949)[23] patents describe the bulk and solution polymerization of *N*-acetyldehydroalanine methyl ester [methyl 2-acetamidoacrylate] to produce a clear, water-soluble homopolymer. Copolymers with acrylonitrile, methyl methacrylate, and styrene were also described. We have applied the methyl ester amide synthesis to isocyanates rather than acid chlorides.[24] *N*-alkyl and *N*-aryl urea monomers are obtained which show excellent radical polymerizability.[25]

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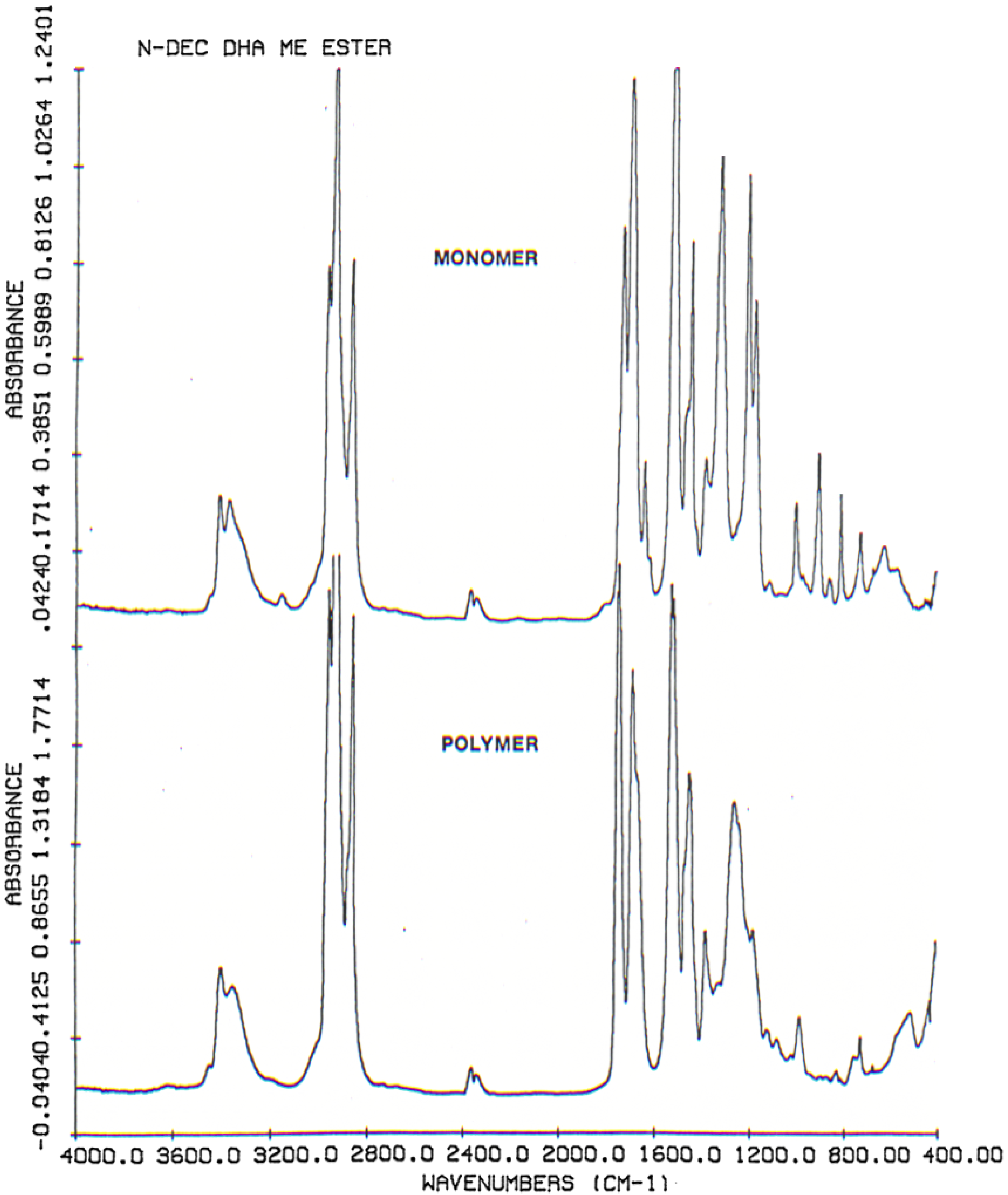
N-DEC DHA ME ESTER
MONOMER
POLYMER
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ABSORBANCE
-0.04040.4125 0.8655 1.3184 1.7714
4000.0 3600.0 3200.0 2800.0 2400.0 2000.0 1600.0 1200.0 800.00 400.00
WAVENUMBERS (CM-1)

Figure 1

## *POLY(N-DECANOYLDEDEHYDROALANINE METHYL ESTER) [POLY(METHYL-2-DECANAMIDOPROPENOATE)]*

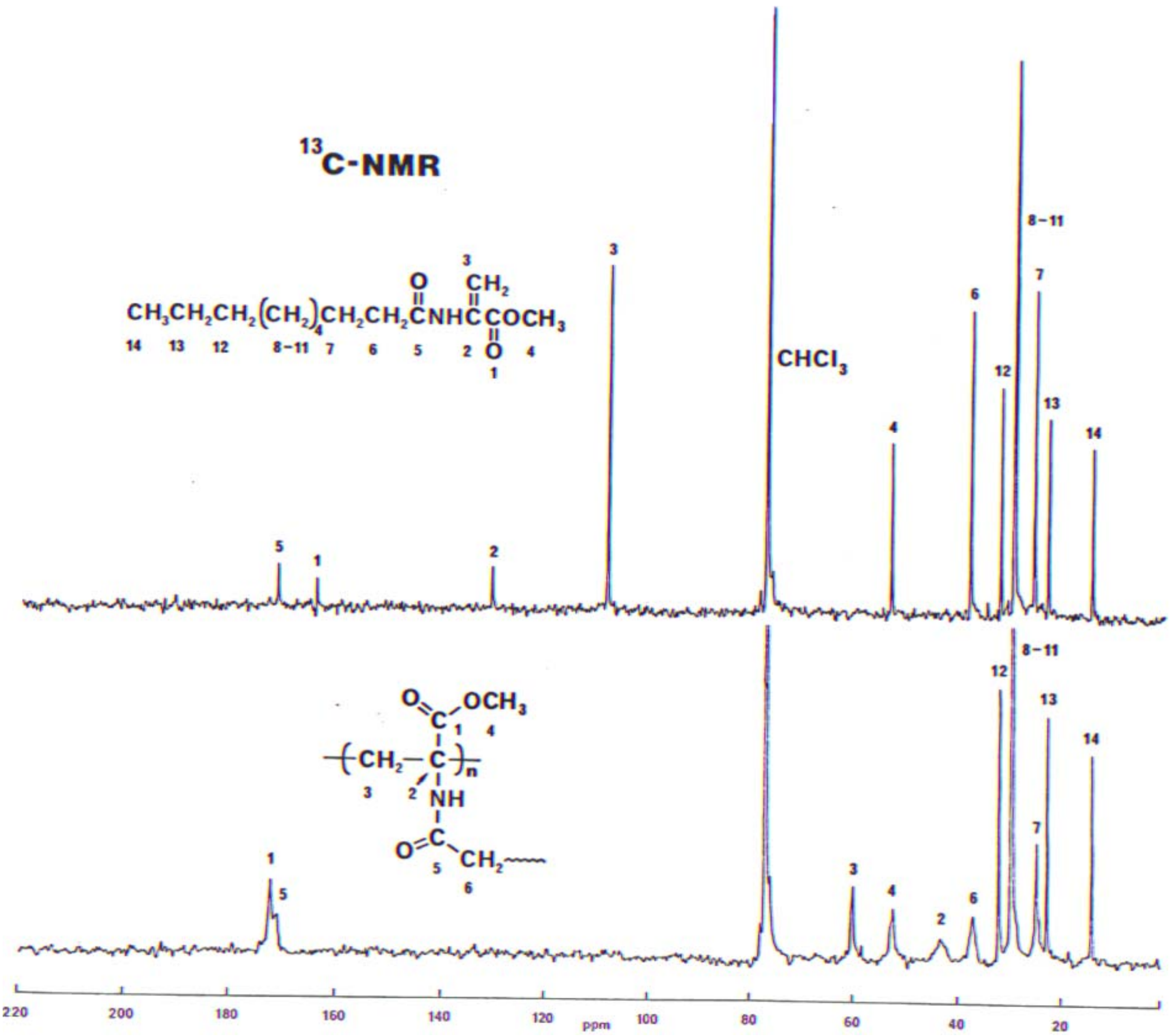
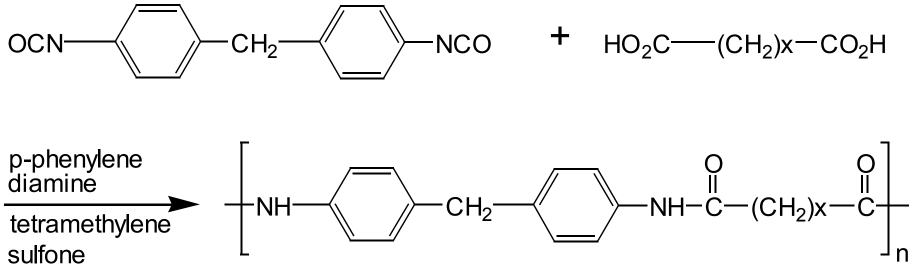


Figure 2

# POLYAMIDES FROM AROMATIC DIISOCYANATES AND DICARBOXYLIC ACIDS

## S.F. Wang and S.J. Grossman[1]

Checked by: B.J. McCarthy and D.A. Tirrell[2]



This type of reaction was first described by Bayer[3] and the reaction conditions were modified by Onder and Grossman.[4]

### 1. Procedure

A dry 250 ml five-neck round bottom flask is placed in a constant temperature oil bath. The flask is fitted with a condenser, a mechanical stirrer (Note 1), an addition funnel, a thermometer and an inlet and outlet for nitrogen gas. To remove air and traces of moisture the flask is flushed with a stream of nitrogen dried by passing it through a 20 cm column of Fisher G-16 mesh silica gel. To this prepared vessel are added azelaic acid (13.16 g, 0.07 mol), adipic acid (4.38 g, 0.03 mol), benzoic acid (0.0452 g as a chain terminator), a catalytic amount of p-phenylene diamine (Note 2) and tetramethylene sulfone (TMSO, 100 g, 80 ml, Note 3). The mixture is stirred and heated to ca 220°C. A solution of 4,4′-diphenylmethane diisocyanate (MDI, 25.0 g, 0.1 mol, Note 4) in TMSO (25 g, 20 ml) is added dropwise over a period of 2 h (Note 5). The residual isocyanate in the addition funnel is rinsed into the reaction flask using more TMSO (10 g, 8.0 ml). After the addition is complete, the reaction mixture is stirred and maintained at the same temperature for 2 additional h. The prepared polymer is recovered by pouring the hot reaction mixture into 2 l of distilled water. The solid precipitate is then chopped by placing the water and precipitate into a stirrer-blender. The chopped strands are then continuously extracted with water using a Soxhlet extractor or by continuous washing with distilled water (Note 6). The solid polymer is then allowed to dry in air followed by 12 h at 90°C under vacuum. A polymer inherent viscosity of 1.0 dl/g is measured for a 0.5% solution in N,N-dimethylformamide (DMF, with 0.5 wt % LiCl, Note 7).

### 2. Methods of Preparation

Aromatic amine based polyamides of high molecular weight can also be prepared by the reaction of dicarboxylic acid chloride and a diamine,[5,6,7] or from the dicarboxylic acid directly using the Yamazaki[8] or Higashi phosphorylation reaction.[9]

### 3. Notes

1. An ACE Trubore stirring shaft, bearing and Teflon stirrer blade permit good stirring of the reaction solution.
2. Catalyst concentration is 0.25-1.00 wt-% of theoretical polymer yield (i.e., 0.084-0.337 g).
3. Freshly distilled tetramethylene sulfone with water content less than 500 ppm must be used which can be obtained by vacuum distillation over a suitable drying agent ($LiAlH_4$).
4. High purity (99%) MDI, e.g. Isonate 125 M (Dow Chemical), should be used. Residual isocyanate dimer is removed by decanting off the pure MDI from a solution of monomer left overnight at 5°C.
5. MDI addition must be metered. Insoluble polymers were obtained when stoichiometric amounts of MDI and acids are combined in one portion.
6. Washing with water is done to remove residual TMSO. This can be checked by thermogravimetric analysis (TGA) which will show residual TMSO as a weight loss at 280-290°C. Residual solvent levels can be lowered to 1-3% by this method.
7. The inherent viscosity is measured at 27°C using an Ubbelohde viscometer (#75) by taking 0.25 g of the reaction mixture (which contains 20% solids) and dissolving it in 10 ml of DMF (with 0.5 wt % LiCl).

## 4. Merits of the Preparation

The attractive features of this reaction include: 1) use of reactants which are tolerant of small deviations in stoichiometric equivalence; 2) easy removal of the volatile condensate, carbon dioxide; 3) high yields of polymer; and 4) generation of a wide range of aromatic polyamides.

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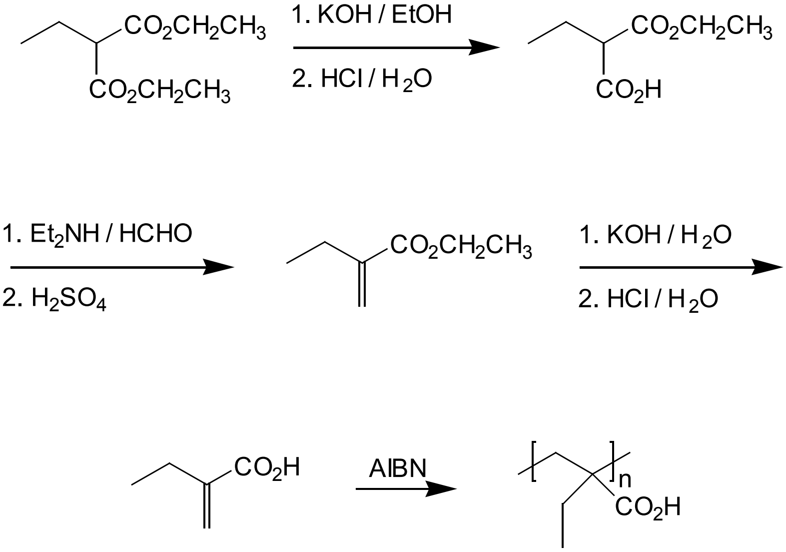
# *POLY(2-ETHYLACRYLIC ACID)*

## M. Ferritto and D.A. Tirrell[1]

Checked by: I.S. Ponticello[2]



## 1. Procedure

### *a. 2-Carboethoxybutyric Acid*

Diethyl ethylmalonate (100 g, 0.53 mol, Note 1) is placed in a 1 l round bottom flask along with 700 ml of 1 M KOH in 95% ethanol. The mixture is allowed to stir overnight (minimum of 12 h). At this point a large amount of white precipitate has formed and is filtered out of solution. The precipitate is placed in a 500 ml Erlenmeyer flask and the filtrate is concentrated on a rotary evaporator. The yellowish oil obtained upon concentration of the filtrate is added to the precipitate. The mixture is dissolved in a minimum amount of water and acidified with dilute aqueous HCl to a pH of 2. An oil separates from the solution. The oil is taken up into diethyl ether and the aqueous layer is extracted three times with 200 ml portions of ether. The ether extracts are combined, dried over magnesium sulfate and filtered. The ether is removed on a rotary evaporator. A quantitative yield (85 g) of crude 2-carboethoxybutyric acid is obtained as a yellowish oil. IR (neat, cm$^{-1}$): 3350-2600, 1740, 1710.

### *b. Ethyl 2-Ethylacrylate*

Crude 2-carboethoxybutyric acid (84.9 g, 0.53 mol) is placed in a 1 l one-neck round bottom flask fitted with a magnetic stir bar and a reflux condenser. The reaction flask is cooled to -5°C and diethylamine is added (55 ml, 0.53 mol, Note 2). An addition funnel is placed on top of the reflux condenser and charged with a formalin solution (43.5 g, 0.54 mol, Note 3). The contents of the addition funnel are dripped slowly into the cooled reaction mixture which is then allowed to warm to room temperature. After stirring for 24 h the reaction mixture is warmed to 60°C and stirred for 8 h more. The mixture now consists of two layers. The reaction mixture is cooled to 0°C and concentrated sulfuric acid is added (Note 4). This mixture is extracted with three 200 ml portions of diethyl ether. The ether extracts are combined, dried over magnesium sulfate and filtered. The ether is removed on a rotary evaporator. Crude ethyl 2-ethylacrylate (47 g, 60%) is obtained as a yellow oil. IR (neat, cm$^{-1}$): 3300-2550, 1725; NMR ($CDCl_3$, *): 5.6 (s, 1H), 6.3 (s, 1H) (Note 5).

### *c. 2-Ethylacrylic Acid*

Crude ethyl 2-ethylacrylate (10 g, 0.078 mol) is placed in a 250 ml one-neck round bottom flask. After 175 ml of 1M aqueous KOH are added, the flask is fitted with a reflux condenser and the reaction mixture is refluxed for 20 h (Note 6). The solution is allowed to cool to room temperature and acidified with dilute aqueous HCl to a pH of 2. An oil separates from the solution and the mixture is extracted four times with 200 ml portions of diethyl ether. The ether extracts are combined, dried over magnesium sulfate and filtered, and the ether is removed on a rotary evaporator. The yellow oil obtained is distilled (bp 55°C/40 mm Hg) to yield pure, colorless 2-ethylacrylic acid (4.7 g, 60% yd). IR (neat, $cm^{-1}$): 3300-2550, 1695; NMR ($CDCl_3$, *): 1.1 (t, 3H), 2.3 (q, 2H), 5.6 (s, 1H), 6.3 (s, 1H), 10.7 (s, 1H).

*d. Polymerization*

2-Ethylacrylic acid (1.00 g, 0.01 mol) is placed in an ampoule with 2,2ℕ-azobis(isobutyronitrile) (AIBN, 0.0328 g, 2 mol%, Note 7). The ampoule is subjected to three freeze-degas-thaw cycles and is sealed under vacuum. The sealed ampoule is heated at 65°C for 12 h cooled, and the resulting slurry poured into excess ethyl acetate. The powdery polymer is separated by filtration, dissolved in methanol and precipitated into diethyl ether. Drying in vacuum at 50-100°C gives poly(2-ethylacrylic acid) (0.71 g, 71% yd, Note 8). NMR ($CD_3OD$, *): 1.1 (m, 3H), 2.1 (m, 2H), 2.3 (m, 2H); IR (neat, $cm^{-1}$): 3700-2700, 1800-1600; $0_{inh}$ (2% in DMF, 30.0°C) = 0.29 dl/g.

## 2. Notes

1. Diethyl ethylmalonate (Aldrich Chemical Co., Milwaukee, WI) is used without purification.
2. Diethylamine (Aldrich) is used without purification.
3. The formalin solution (Fisher Scientific) is a 37% aqueous formaldehyde solution and is used without purification.
4. Caution! A violent reaction occurs upon addition of $H_2SO_4$ to the reaction mixture. The violent reaction is accompanied by the evolution of a small volume of gas. The $H_2SO_4$ should be added slowly until the violent reaction no longer occurs upon further addition.
5. Since the crude product is not purified for the next step, the presence of the olefinic protons in the NMR spectrum is used to confirm the intermediate structure.
6. Ethyl 2-ethylacrylate is insoluble in aqueous KOH, but the potassium salt of 2-ethylacrylic acid is soluble. Refluxing of the solution should therefore be continued until the mixture is homogeneous. This step can be shortened to 2 h by the addition of 1 ml of a 50% aqueous solution of tetrabutylammonium hydroxide (available from Aldrich).
7. 2,2ℕ-Azobis(isobutyronitrile) (AIBN, Aldrich) is recrystallized from methanol with care not to warm the solution above 45°C. The white crystals are dried in a vacuum desiccator before use.
8. Other solvent-nonsolvent systems that can be used to reprecipitate poly(2-ethylacrylic acid) are N,N-dimethylformamide (DMF)-ethyl acetate and pyridine-aqueous HCl.

## 3. Methods of Preparation

2-Ethylacrylic acid has been synthesized by reaction of diethyl ethylmalonate with formaldehyde followed by hydrolysis, dehydration and decarboxylation.[3]

2-Ethylacrylic acid can be solution polymerized in an aqueous solvent. Polymerization has been achieved using a 5.3% aqueous solution of the monomer initiated by 1% $K_2S_2O_8$ and 0.25% $NaHSO_3$ (w/w to the monomer).[4,5] Polymerization has also been carried out by using a 5% aqueous solution of the monomer initiated by 2,2'-azobis(isobutyramidine)-hydrochloride at about 0.5% (w/w to the monomer).[6] Both solution polymerization reports suggest the mixtures be heated for two days. The bulk polymerization of 2-ethylacrylic acid described here requires 12 h and gives pure, white polymer in good yield and in a powder form that is easily handled.

## 4. References

1. Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003.
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# POLY( L-ORNITHINE HYDROGENBROMIDE)

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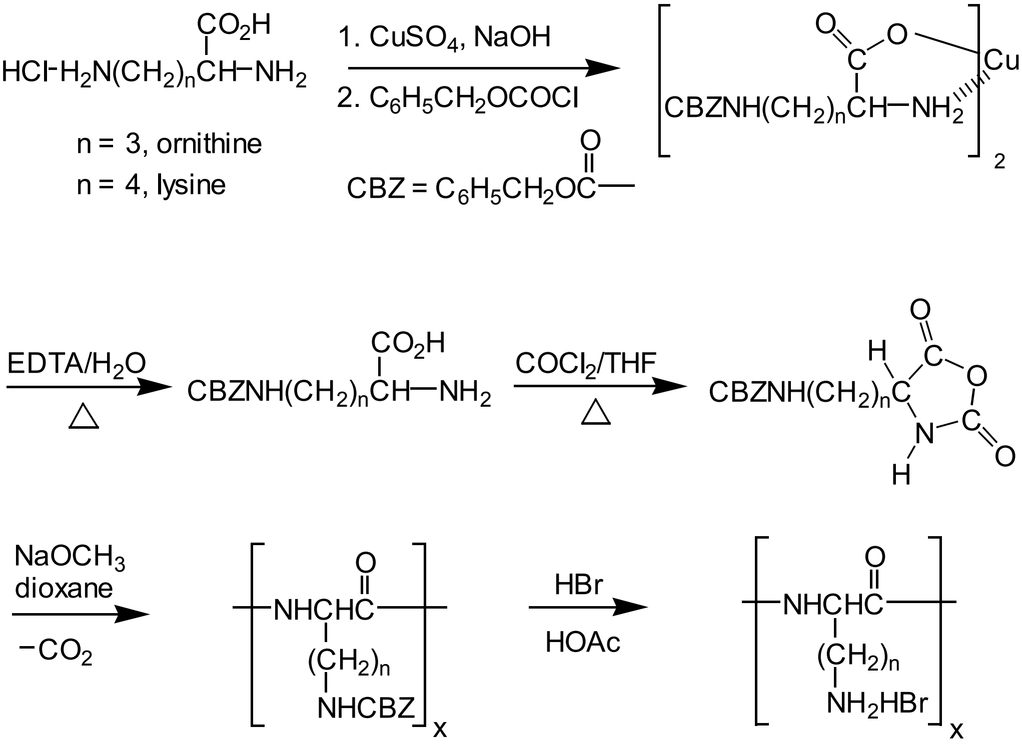
Checked by: H. Creel and D.A. Tirrell[2]



## 1. Procedure

### *a. $N_*$-Carbobenzoxy-L-ornithine, Copper Complex*

To a well stirred solution of NaOH (96.0 g, 2.40 mol) in $H_2O$ (2.10 l) in a 12 l round-bottom indented flask is added L-ornithine monohydrochloride (202.8 g, 1.20 mol). A solution of $CuSO_4$-$5H_2O$ (151.2 g, 0.60 mol) in $H_2O$ (2.10 l) is added in several portions and the resulting inky blue solution cooled to 10°C in an ice/water bath. Benzyl chloroformate (220 ml, 263 g, 1.54 mol) and 2.0 M NaOH (0.60 l, 1.20 mol) are concurrently added dropwise, maintaining the pH at 9-10 and the internal temperature at 8-10°C. After the addition is complete (ca 90-120 min), the reaction mixture is allowed to warm to room temperature and stirred overnight. The blue sand-like precipitate is filtered (Note 1) and washed with $H_2O$ (6.0 l), then gently slurried in ethanol (2.0 l, Note 2) and refiltered. The precipitate is washed with ether (2.0 l) and air dried for 1 h, then dried in a vacuum oven at 80°C to constant weight to give the carbobenzoxy (CBZ) derivative complex; yd 325 ± 5 g, 90-92% (Note 3).

### *b. $N_*$-Carbobenzoxy-L-Ornithine*

To a well stirred solution of ethylenediaminetetraacetic acid (75.0 g, 0.25 mol) in boiling $H_2O$ (10.0 l) in a 22 l round-bottom flask with a bottom stopcock is added $N_*$-CBZ-L-ornithine copper complex (150.0 g, 0.25 mol) in several portions. The resulting deep blue solution is stirred at 100°C for 45 min then drained through the bottom outlet of the flask through a polyethylene mesh into a receiving flask (Note 4). The reaction mixture is allowed to cool to room temperature overnight, depositing the title compound as fluffy white crystals. The product is filtered and washed with $H_2O$ (10 l), slurried in $H_2O$ (10 l), filtered again and washed with $H_2O$ (6 l) (Note 5). The product is dried to constant weight in a vacuum oven at 80°C to give white powder; mp (dec) 252-254°C (yd 101 g, 84%).

### *c. N$_*$-Carbobenzoxy-N$_{''}$-carboxy-L-ornithine Anhydride*

**CAUTION: This procedure uses phosgene, a deadly gas. All manipulations must be carried out in an efficient hood.**

N$_*$-CBZ-L-Ornithine (300 g, 1.12 mol) is added to tetrahydrofuran (2.2 l) in a 4-neck, 22 l round-bottom indented flask equipped with an overhead stirrer, thermometer, and drying tube filled with Drierite. Phosgene is added (Fluka, 20% in toluene; 1.00 l, 1.93 mol) and the mixture stirred at 50-60°C with a hot water bath until dissolution is achieved (ca 1 h). Stirring is continued at this temperature for 15 min, then the water bath is removed and light petroleum ether (bp 35-60°C, 8.5 l) is added via peristaltic pump to precipitate the crude product as an off-white, sometimes gummy solid. The supernatant is drawn off via peristaltic pump, then the precipitate is filtered, washed with light petroleum ether and dried at reduced pressure to give a granular, off-white powder **(Caution: powder may contain residual phosgene)**. The filtrate and supernatant are treated with ammonia to destroy any excess phosgene before being discarded. The crude product is dissolved in ethyl acetate (700 ml), treated with decolorizing carbon (Note 6) and clarified by filtration through Celite (Note 7) to give a clear, almost colorless solution. This is cooled in an ice bath and light petroleum ether (800 ml) is added with efficient stirring to effect recrystallization. The product is filtered, washed with petroleum ether and dried under reduced pressure to give 240-250 g (72-76% yd) of the title compound; mp (dec) 90-91°C. The product slowly decomposes at room temperature and must be stored in a freezer at -40°C until needed.

### *d. Poly(L-Ornithine Hydrogenbromide)*

An initiator solution is prepared by dissolving sodium methoxide (20.0 g, 0.37 mol) in dry dioxane (40 ml, Note 8) and dry methanol (60 ml, Note 9) under nitrogen in a flame-dried 500 ml round-bottom flask (Note 10). In a four-neck, 12 l indented round-bottom flask fitted with thermometer, overhead stirrer, nitrogen inlet and septum, N$_*$-carbobenzoxy-N$_{''}$-carboxy-L-ornithine anhydride (586 g, 2.0 mol) is dissolved in dry dioxane (3.00 l) and the internal temperature is adjusted to 17-18°C with a water bath at 15-17°C. With vigorous stirring the initiator solution is injected over a period of 60 sec using a 100 ml syringe. The internal temperature rises 6-7°C over 4-5 min after injection. The reaction mixture is stirred for 2 h, although evolution of $CO_2$ ceases after ca 15 min (Note 11).

A solution of hydrogen bromide in acetic acid (7.5 l, 30-35% w/w) is prepared in a 22 l jacketed flask equipped with overhead stirrer, drying tube and bottom drain, and the polymerization reaction solution added with vigorous stirring. The deprotected polymer salt begins to precipitate in 4-5 min, but evolution of $CO_2$ continues for 2 h at which time ether (8.0 l) is added to complete the precipitation (Note 11). The crude polymer is collected in a 32 cm Büchner table funnel, washed with a 1:1 mixture of acetone and ethanol (2 l), then slurried in 1:1 acetone/ethanol (3 l) with ice bath cooling. When the suspension becomes homogenous (ca 15 min) it is filtered, the precipitate dissolved in water (1.60 l), and the aqueous solution transferred to a 22 l, 4-inch-neck indented round-bottom flask. With vigorous stirring, 1:1 ethanol/acetone (10 l) is added via peristaltic pump to precipitate the polymer. As much as possible of the supernatant is decanted (ca 10 l), ethanol (1.5 l) is added and the polymer is slurried for 15 min. The spongy precipitate is filtered, put into a 5 l indented round-bottom flask and slurried overnight in ethanol (1.5 l). The polymer is filtered, washed with ether (1.0 l) and dried at 80°C/0.5 torr for 8 h to give the polymer as a hygroscopic white granular powder (280 ± 5 g, 70-74% overall yd).

## 2. Characterization

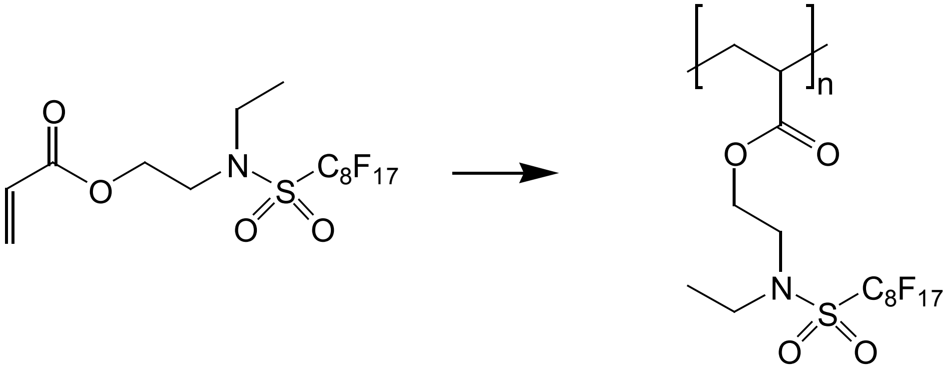
N$_*$-Carbobenzoxy-L-ornithine has mp (dec) 252-254°C (lit. mp 254-256°C[3], 253-255°C[4]) and is checked for purity by thin-layer chromatography (TLC) using n-butanol/acetic acid/water 3.5/1/1, silica gel, ninhydrin visualization, $R_F$=0.47, one spot.

N$_*$-Carbobenzoxy-N$_{''}$-carboxy-L-ornithine anhydride is a white powder, mp (dec) 90-91°C (lit. mp 86°C[3]). The infrared spectrum (KBr) exhibits absorptions at 3319, 2938, 1848, 1805, 1758, 1688, 1534 and 1254 $cm^{-1}$. The 60-MHz NMR spectrum ($CDCl_3$) is characterized by peaks at * 1.5-2.1 (m, 4, $, ($-CH_2$), 3.26 (t, 2, J=6Hz, *-$CH_2$), 4.35 (t, 1, J=2Hz, CH); 5.13 (s, 2, $CH_2O$), 7.05 (m, 1, NH), and 7.35 (s, 5, $C_6H_5$) (Note 12). TLC in benzene/acetone 1:1, silica gel, $I_2$ or ninhydrin visualization, $R_F$=0.52, showed some streaking due to decomposition on the plate.

# *POLY( N- ETHYL PERFLUOROOCTANE SULPHONAMIDO ETHYL ACRYLATE)*

## R. Ramharack[1]

Checked by: R.W. Stackman and S.M. Hurley[2]



## 1. Procedure

*a. Thermal Polymerization*

EtFOSEA (5.0 g, 7.6 mmol, Notes 1 and 2) is dissolved in 15 g of distilled trichlorotrifluoroethane (Freon™ 113, Note 3) in a 4 oz borax bottle. The initiator, bis-(4-tert-butylcyclohexyl) peroxydicarbonate (0.041 g, 0.11 mmol, Note 3), is added and dissolved. The reaction mixture is flushed with $N_2$, quickly capped and taped with black electrical tape. The bottle is then placed in a hot water bath (60°C) in the hood for 4 h. The solution becomes quite viscous. The polymer is precipitated by dropwise addition to methanol (Note 4). This is done twice. The polymer is filtered to obtain a white powder and then vacuum dried at 60°C for 24 h. The white powder (yd 90-98%) is analyzed by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and size-exclusion chromatography (SEC).

*b. Photopolymerization*

EtFOSEA (5.0 g, 7.6 mmol) is dissolved in 15 g of trichlorotrifluoroethane in a 4 oz borax bottle. The initiator, 2,2'-azobis(isobutyronitrile) (0.045 g, 0.27 mmol, Vazo™ 64 obtainable from the DuPont Company) is added. The reaction mixture is flushed with $N_2$, quickly capped and taped as above. It is then placed six inches from fluorescent UV black lamps (General Electric, 15 watts) for 4 h (Notes 5 and 6). The bottle is removed and the polymer is recovered and purified as described above; yd 75%.

## 2. Characterization

The polymers are insoluble in hydrocarbon solvents. However, they are soluble in Freon™ 113 and ",",",-trifluorotoluene (TFT, Note 7). The surface energies are found to be quite low (10-13 dynes-cm$^{-1}$).[3] For poly(EtFOSEA) the DSC shows a $T_g$ at ca 34°C and a melting transition at ca 74°C.[4] The size exclusion chromatography (SEC) is done using TFT as solvent[4] (Note 7) to give values relative to polystyrene in tetrahydrofuran. The thermal polymerization gives a polymer of $M_n$ = 81,407 and $M_w$ = 174,483. The photopolymerization gives a polymer of $M_n$ = 208,175 and $M_w$ = 333,370 (Note 8).

## 3. Notes

1. The Industrial Chemical Products Division of the Minnesota Mining and Manufacturing Company (3M) offers a series of monomers of generic formula $CH_2{=}C(R_1)C(O)O(CH_2)_nN(R_2)SO_2C_8F_{17}$. For $R_1$=H, n=2 and $R_2$=ethyl, the monomer is N-ethyl perfluorooctane sulphonamido ethyl acrylate (EtFOSEA) sold as Fluorad FX-13.
2. The monomers are waxy solids that are very soluble in hydrocarbon solvents such as tetrahydrofuran, toluene, ethyl acetate, 2-butanone, acetone and methanol. A 90/10 methanol/water mixture is a very good recrystallizing solvent to free the monomers of impurities and inhibitors (phenothiazine and p-

methoxyphenol). The recrystallized monomers are chalk-white crystals with sharp melting points. The melting point of EtFOSEA is 38-39$^{o}$C. The checkers recrystallized twice from methanol alone to a melting point of 42.5-43.5$^{o}$C.

3. Trichlorotrifluoroethane is obtained as Freon™ 113 from the E. I. DuPont Company. ",",",-Trifluorotoluene (TFT) is obtainable from Aldrich Chemical Company and also works well as the polymerization solvent. Bis-(4-tert-butylcyclohexyl) peroxydicarbonate is obtainable as Percadox™ 16N from the Noury Corporation.
4. The checkers suggest pouring the reaction mixture into methanol in a Waring Blender.
5. VAZO™ 64 does function as a good UV initiator. It is somewhat surprising to us that the polymerization is fairly fast even though we used borax glass.
6. The checkers tried unsuccessfully to induce photopolymerization with a 6 watt black lamp. Irradiation for 12 h with a Gates mercury lamp of intensity 64 watts/in$^{2}$ afforded a 94% yield of white, fibrous polymer.
7. Freon™ 113 cannot be used as a SEC solvent as it is too volatile. Spectroscopic grade TFT is treated with a small quantity of ethanol and filtered to remove traces of HF and used as the SEC solvent.
8. The checkers found the polymers to be incompletely soluble in TFT. Viscosity measurements were performed in trichlorotrifluoroethane and gave inherent viscosities of 0.20 and 0.28 dl/g for the products of thermal and photopolymerizations, respectively.

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# HOMOPOLYMERIZATION OF ALKYL α- (HYDROXYLMETHYL)ACRYLATES

## L.J. Mathias, A.O. Kress and S.H. Kusefoglu[1]

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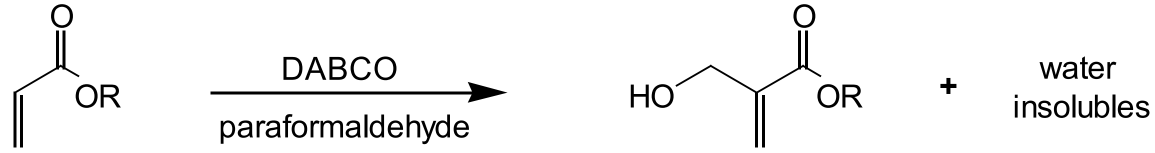

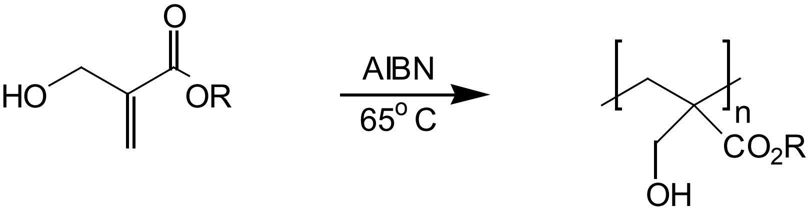

### 1. Synthesis of alkyl "-(hydroxymethyl)acrylates

Ethyl acrylate (285.3 g, 2.88 mol), paraformaldehyde (32.5 g, 1.08 mol) and 1,4-diazobicyclo[2.2.2]octane (DABCO, 6.5 g, 2.0% w/w) are stirred at room temperature. The reaction is monitored by gas chromatography (Note 1) and terminated after 19 days to give approximately 18% ethyl "-(hydroxymethyl)acrylate (EHMA) and 4.0% of the ether dimer, bis(ethoxycarbonyl-2-propenyl) ether.[3] The reaction may be carried out at elevated temperature (ca 60°C) to speed up conversion to ca 30-35% EHMA in 8-10 h. However, since the rate of ether formation is also increased by both higher temperatures and higher concentrations of EHMA, GC monitoring is vital to ensure maximum yield of EHMA with minimum loss to the ether dimer. If the dimer is the desired product, elevated temperature is desirable (see next procedure).

Unreacted ethyl acrylate is removed under reduced pressure and any residual paraformaldehyde is removed by filtration. The crude mixture is washed with dilute HCl and the aqueous solution extracted with diethyl ether. The combined ether fractions are dried ($Na_2SO_4$), added to the organic phase, concentrated in vacuo and fractionated under reduced pressure. Cuprous chloride (or any available inhibitor such as the benzoquinone or hydroquinone derivative) is added in small amounts.

Fraction 1, bp 58-59°C/0.35 mm Hg is predominately EHMA. Fraction 2, bp 100-104°C/0.2 mm Hg is predominately bis(2-carboethoxy-2-propenyl) ether. Fraction 3, bp 140-146°C/0.15 mm Hg is a mixture of acetals of EHMA and formaldehyde.

Fraction 1 is redistilled giving EHMA as a clear, free-flowing liquid. Redistilled fraction 2 gives bis(2-carboethoxy-2-propenyl) ether as a slightly viscous clear liquid. The ether dimer and diacrylate acetals are good crosslinkers[4] and must be removed from the EHMA if soluble polymers and copolymers are desired.

These monomers and dimers may be stored in the refrigerator at 0-5°C for a few days, but will spontaneously polymerize even at these temperatures. Inhibitor should be added for prolonged storage; any of the commercial acrylate inhibitors may be used including the monomethyl ether of p-hydroquinone.

Methyl "-(hydroxymethyl)acrylate (MHMA) may be prepared (not recommended) in a similar manner[5] although the monomer (or a readily-formed by-product from its synthesis) is a powerful skin irritant which causes blisters and contact dermatitis on exposure to the vapor. **CAUTION** is required in its synthesis: a good hood, butyl rubber gloves and extreme care.

## 2. Monomer Characterization

The alkyl "-(hydroxymethyl)acrylates are clear liquids having somewhat pungent odors. Preliminary skin irritancy tests show the pure compounds to be comparable to alkyl acrylates except for MHMA which causes contact dermatitis.

The IR spectra generally have absorption bands in the following regions: OH stretch at about 3400, carbonyl peak at 1710, and weak double bond absorption at 1610 cm-1. The 200 MHz $^1$H NMR spectrum in CDCl$_3$ at room temperature shows alkene proton peaks at 6.2 and 5.8 ppm, the OH peak at about 4.5 ppm, and the methylene hydrogens " to the OH at 4.0 ppm (depending on concentration and dryness). The 50 MHz $^{13}$C NMR spectra in CDCl$_3$ at room temperature has peaks for the carbonyl at 165 ppm, the alkene carbons at 140 and 125 ppm, and the " OH methylenes at 62 ppm. Ether by-products show an easily-seen CH$_2$-O peak at ca 68 peak which allows qualitative and quantitative evaluation of the amount of ether dimer present in crude or distilled monomers. Ester group hydrogen and carbon peaks appear at characteristic chemical shifts.

## 3. Procedure 1 (Bulk Polymerization)

Ethyl "-(hydroxymethyl)acrylate (EHMA, 2.26 g, 17.4 mmol) and 2,2'-azobis(isobutyronitrile) (AIBN, 40.0 mg, 1.7% w/w, Note 2) are sealed in a 2-dram vial equipped with a rubber septum, degassed three times using a freeze-thaw method, and then heated at 65°C for 12 h. A solid mass forms during this time. The sample is cooled, dissolved in chloroform, acetone or 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP, Note 3), and precipitated by addition to diethyl ether. This procedure is repeated twice giving poly(EHMA) as a white powder which is then dried at 50-80°C under vacuum; higher temperatures may cause transesterification and crosslinking.

## 4. Procedure 2 (Solution Polymerization)

Ethyl "-(hydroxymethyl)acrylate (1.027 g, 7.9 mmol), AIBN (21.1 mg, 2% w/w) and ethyl acetate (10 ml) are sealed in a 20-ml vial equipped with a rubber septum, degassed three times using a freeze-thaw method and then heated to 60°C for 12 h. During this time the viscosity of the solution does not increase to any significant extent. The reaction mixture is cooled to room temperature, precipitated by addition to diethyl ether and filtered. The product is redissolved and reprecipitated by addition to diethyl ether. This procedure is repeated twice to give low molecular weight poly(EHMA) as a white powder which is dried at 110°C under vacuum. Yields are 195-240 mg (19-23%).

## 5. Polymer Characterization

Poly(MHMA) is only soluble in HFIP while poly(EHMA) is soluble in HFIP, dimethylsulfoxide, N,N-dimethylacetamide, tetrahydrofuran, dimethylformamide, N-methylpyrrolidone, ethyl acetate, chloroform and acetone. Poly(EHMA) is slightly soluble in ethanol and methanol, and insoluble in carbon tetrachloride, water, benzene and diethyl ether. The presence of even small amounts of the ether dimer gives crosslinked and insoluble products. The poly(EHMA) obtained by bulk polymerization has an intrinsic viscosity (Note 4) of 0.18 dl/g in acetone at 25°C and 0.32 dl/g in DMSO at 25°C. (The checkers obtained values of 0.18 and 0.28 dl/g, respectively.)

The IR spectrum (Note 5) shows the following absorption bands for poly(MHMA): 3452 (OH stretch), 2959 (CH stretch), 1737 (C=O stretch), 1442, 1401, 1245, 1163 and 1040 cm$^{-1}$. The 200 MHz $^1$H NMR spectrum (Note 6) in DMSO-d$_6$ at room temperature for poly(MHMA) gives broad peaks at 4.8 (OH), 3.3 (methoxy absorption), and 2.1 (methylene absorption) ppm from TMS. The 50 MHz $^{13}$C NMR spectrum in DMSO-d$_6$ for poly(EHMA) at room temperature has peaks at the following positions: 173.7-174.2 (carbonyl); 60.1-60.9 ("-CH$_2$OH and ester "-methylene); 13.5 (methyl of ester group); and 42 and 50 ppm (broad backbone peaks centered at these values).

A glass transition of 145°C is found for poly(MHMA), and 96°C for poly(EHMA) solution and bulk polymer as determined by differential scanning calorimetry (Note 7). Repeated DSC scans and drying at too high a temperature cause thermal lactonization and transesterification which lead to higher T$_g$ and crosslinked polymers.

## 6. Notes

1. Gas chromatography is run on an HP 5880 level 4 system equipped with FID detectors and a 5% phenyl methyl polysiloxane fused silica open tubular capillary column.
2. AIBN is recrystallized from methanol, dried under vacuum and stored in a desiccator until used.
3. HFIP is corrosive and irritating, and requires extreme care.
4. A Cannon-Ubbelohde #50 semi-micro viscometer is used.
5. A Nicolet 5DX FTIR is used to obtain the infrared spectra.
6. A Bruker MSL-200 is used to obtain the NMR spectra.
7. A DuPont 9900 computer equipped with a DuPont 910 DSC unit is used for thermal analysis.

## 7. Methods of Preparation

MHMA is prepared by the action of paraformaldehyde and methyl acrylate in the presence of DABCO.[6] MHMA and EHMA are also prepared by carboxylation of propargyl alcohol followed by esterification,[7,8] and by the reaction of alkyl acrylate and formalin in the presence of DABCO.[9] Additionally, EHMA is prepared by the action of mineral acid on bis(hydroxymethyl)malonate followed by esterification,[10] and by Wittig-Horner reaction of triethylphosphonoacetate with formaldehyde.[11,12,13,14]

Most of the above procedures suffer from a variety of drawbacks such as drastic reaction conditions, toxicity of reagents, poor yields, difficulties in obtaining reagents, and/or formation of by-products and impurities leading to poor polymerizability. While yields with our procedure are not high, materials obtained are easily purified, and recovered starting materials may be recycled. Generality is demonstrated by the fact that other ester derivatives have been prepared including the n-butyl (BHMA) and t-butyl (TBHMA) monomers. The latter and its polymer are readily converted to the free acid derivatives by treatment with trifluoroacetic acid.[15]

EHMA has been the subject of a number of polymerization and copolymerization studies,[16,17,18,19] although MHMA has apparently not been deliberately polymerized previously. The multifunctionality of these monomers makes available a variety of additional monomer derivatives and functionalized polymers. Radical polymerization gives the homopolymers (as reported here) with pendent alkoxycarbonyl and methylol groups which can be lactonized, crosslinked or chemically modified in a variety of ways. Copolymerization is facile with MHMA and EHMA showing reactivity ratios comparable to those of methyl methacrylate with styrene.[20,21]

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# SYNTHESIS AND CYCLOPOLYMERIZATION OF BIS(2-ALKOXYCARBONYL-2-PROPENYL) ETHER

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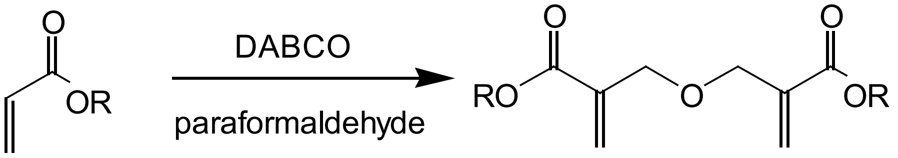
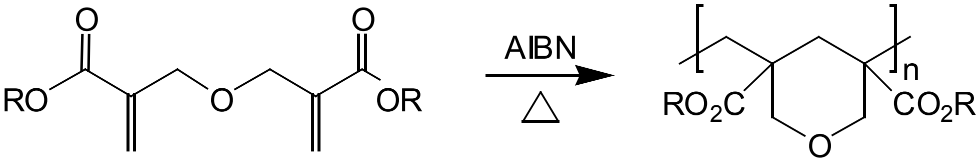
Checked by: M.S. Ferritto and D.A. Tirrell[2]





## 1. Synthesis (Ethers)

Bis(2-alkoxycarbonyl-2-propenyl) ethers may be obtained as major by-products in the DABCO catalyzed synthesis of the alkyl "-(hydroxymethyl)acrylates[3] (see previous method, this volume). Alternatively, they may readily be prepared in good yield directly from the acrylate by allowing the hydroxymethylation reaction and subsequent ether-forming dimerization to proceed to completion. The following method is typical.

Ethyl acrylate (20.0 ml, 0.188 mol), paraformaldehyde (2.82 g, 0.0957 mol), 1,4-diazabicyclo[2.2.2.]octane (DABCO, 1.05 g, 0.0094 mol) and a teflon-coated stirring magnet are charged to a 20 oz. Quorpak wide-mouth jar with polyethylene lined phenolic cap. Excess ethyl acrylate is used as solvent. All reagents were used as received from Aldrich Chemicals.

It has been found that submerging the closed reaction vessel in the heating medium[4] is necessary to avoid vaporization and subsequent recondensation of the formaldehyde out of the reaction medium. This also avoids DABCO catalyst deposition at the edge of the reaction solution as the ether product concentration increases due to decreased solubility.

The jar is sealed and submerged in an oil-bath which is then heated to approximately 70°C. After three days the vessel is removed and its contents added to 30 ml diethyl ether. The organic solution is then washed with a solution of 1% aqueous HCl (3 times, 10 ml each). The aqueous layer is back-extracted with 10 ml diethyl ether. Organics are combined, and solvents and unreacted ethyl acrylate removed using a rotary evaporator. A large pinch of copper(II) chloride is added as a free-radical inhibitor and the solution fractionally distilled to produce 5.8 g of 91% pure bis(2-ethoxycarbonyl-2-propenyl) ether (yield 50%, Note 1).

The ethyl derivative is a liquid (bp 101-102°C at 0.2 mm Hg) while the methyl derivative is a solid (mp 48°C) that is readily recrystallized from methanol or pentane.[5] The n-butyl and t-butyl compounds boil so high, even under vacuum, that they are difficult to distill without spontaneous polymerization. However, extraction and distillation to remove catalyst and all by-products generally leaves the ether as the only product left in the distillation flask. Copper(II) chloride (or other inhibitor) should be added for vacuum distillation and storage of the crude reaction mixtures and purified ethers.

## 2. Characterization (Ethers)

Bis(2-alkoxycarbonyl-2-propenyl) ethers are readily soluble in DMSO, chloroform, and methylene chloride; slightly soluble in pentane and methanol; and insoluble in water. The infrared spectrum for the methoxycarbonyl derivative exhibits the following absorption bands [cm-1]: 2980-2870 (CH stretch), 1716 (carbonyl stretch), 1636 (C=C stretch), 1463 (asymmetric CH$_2$ bend), 859 (C=CH$_2$ out-of-plane bend), and 1111 (R-O-R stretch). Other derivatives display essentially identical spectra except for increased intensity for the alkane peaks.

The proton spectrum of the ethoxycarbonyl derivative in CDCl$_3$ shows alkene proton singlets at * 6.29 and 5.90; a 2-proton singlet at 4.26 attributed to the ether "-methylene; a 2-proton quartet at 4.13 attributed to the ester methylene; and a 3-proton triplet at 1.30 attributed to the ester methyl. The carbon spectrum of this monomer shows a carbonyl at * 165.7; alkene peaks at 137.6 and 125.3; and peaks for the ether methylene (69.0), ester methylene (60.7), and ester methyl (14.2). The C-H coupled spectrum confirms these assignments.

## 3. Cyclopolymerization

Bis(2-methoxycarbonyl-2-propenyl) ether (10.16 g, 47.5 mmol), 2,2'-azobis(isobutyronitrile) (AIBN, 640 mg, Note 2) and chloroform (240 ml, Note 3) are placed in a capped round-bottom flask and degassed by bubbling nitrogen through the solution. The mixture is then heated at 65°C for 6 h to give a clear solution having only a small quantity of insoluble material.

The solution is cooled in an ice bath, insolubles removed by filtration (0.09 g, 0.9%), and the filtrate slowly added to diethyl ether to give the cyclopolymer as a white precipitate. The polymer is purified by repeated dissolution, precipitation, washing and drying under vacuum. The yield of soluble polymer is 8.8-9.6 g, 87-95%.[6] The cyclopolymers of bis(2-ethoxycarbonyl-2-propenyl) ether and bis(2-n-butoxycarbonyl-2-propenyl) ether are prepared in a similar manner. The monomeric t-butyl ester dimer spontaneously gave soluble, high molecular weight cyclopolymer on attempted distillation. This polymer can be readily converted to the free acid material by treatment with neat trifluoracetic acid.[7]

## 4. Characterization (Cyclopolymers)

The cyclopolymers are soluble in chloroform and 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP, Note 4) and insoluble in diethyl ether except for the t-butyl ester polymer which is soluble in diethyl ether and petroleum ether. The intrinsic viscosities in chloroform (Note 5) are 0.15 to 0.45 dL/g. (The checkers obtained a value of 0.21 dL/g).

The infrared spectrum (Note 6) for the methoxycarbonyl polymer exhibits the following absorption bands [cm-1]: 3009-2861 (CH stretch), 1745 (carbonyl stretch), 1261 and 1171 (ester C-O-C stretches). The 50 MHz carbon NMR spectrum (Note 7) in CDCl$_3$ at room temperature of the methoxycarbonyl polymer shows absorptions at [*]: 173.5, 172.9 (carbonyls), 71.2 (CH$_2$O), 51.4 (OCH$_3$) and 43.5 (backbone). Nutation NMR analysis of a dimer labeled with $^{13}$C confirms formation of the 6-membered ring pyran structure rather than the tetrahydrofuran possibility.[8]

TGA thermograms (Note 8) display two weight loss transitions, one at 200°C apparently due to residual solvent desorption, and a second at about 300°C involving catastrophic weight loss through depolymerization and degradation. The DSC thermogram for the methoxycarbonyl polymer shows a strong glass transition at about 160°C while that of the t-butyl polymer is 136°C. Decomposition onset occurs at 270°C for the former and ca 180°C for the latter.

## 5. Notes

1. Purity is determined by gas chromatography using a Hewlett Packard 5890A gas chromatograph with HP3396A integrator and J & W 5% phenyl methyl polysiloxane column. Yield is based on initial paraformaldehyde concentration.
2. AIBN is purified by recrystallization from methanol.
3. Benzene and acetone may give insoluble polymers.
4. HFIP is a corrosive material and should be used with care.
5. A Cannon-Ubbelohde #50 semimicro viscometer is used.
6. A Nicolet 5DX FTIR is used to obtain the infrared spectra.

7. A Bruker MSL-200 is used to obtain $^{1}H$ and $^{13}C$ NMR spectra.
8. A DuPont 9900 thermal analyzer equipped with a DuPont 910 DSC and a DuPont 951 TGA is used to obtain thermograms.

## 6. Method of Preparation

Free-radical cyclopolymerizations are well known.[9,10] A study of cyclopolymerization in a number of solvents of different dielectric constants has been published.[11] Intramolecular cyclization reactions were first discovered by Butler and co-workers who found that the radical polymerization of quaternary diallylammonium salts gives soluble, uncrosslinked polymers.[12]

The products synthesized in this report are related to DIVEMA, a cyclopolymer of divinyl ether and maleic anhydride. DIVEMA shows a broad range of biological activity:[13,14] it acts as an antitumor agent, an antiviral agent, an antibacterial and antifungal agent; it stimulates immune system response; and it acts as an anticoagulant. DIVEMA does suffer from some disadvantages: its molecular weight distribution is hard to control, and it may posses a microstructure which includes furan as well as pyran ring structures. Although a 1:2 repeat unit is reported for DIVEMA, other ratios of comonomers scattered along the backbone may be present, leading to configurational and compositional inhomogeneities.

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# Alternating Ether-Thioether Polymers by Michael Addition of Dithiols and Bis(2- Alkoxycarbonyl-2-Propenyl) Ether

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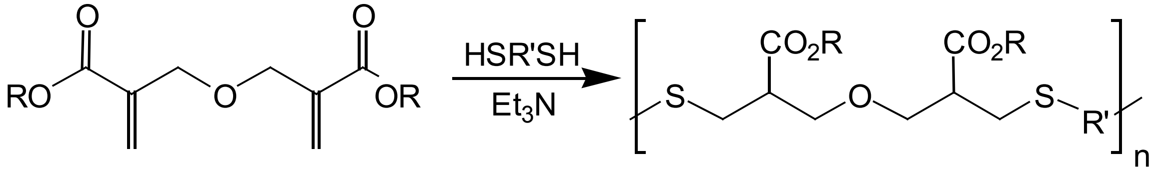

R' = $(CH_2)_{2,3,4,6}$ or $CH_2CH_2XCH_2CH_2$
with X = O or S

## 1. Procedure (Note 1)

A small tube containing bis(2-alkoxycarbonyl-2-propenyl) ether (369.6 mg, 1.53 mmol, Note 2), $,$N-dimercaptoethylsulfide (233.0 mg, 1.51 mmol, Note 3) in $CHCl_3$ or $CDCl_3$ (approximately 1 ml) is treated with anhydrous triethylamine (19.0 mg, 3.1% w/w, Note 4) in a slightly exothermic reaction. The viscosity increases dramatically within 1 h of addition of the amine.

The reaction is monitored by $^{13}$C-NMR (Note 5) and additional reactants are added as needed. The reaction is continued until little or no reactants are observed.

The contents of the reaction tube are decanted into a round bottom flask along with wash chloroform to effect complete transfer. The sample is concentrated in vacuo to give a clear, highly viscous liquid. The residue is dried under high vacuum and triturated with diethyl ether. The ether-soluble material is decanted and the residue dried under vacuum to give the product as a clear, highly viscous liquid. The yield is 477 mg (76% of theoretical).

## 2. Characterization

The thioether polymers synthesized by this procedure are soluble in chloroform and methylene chloride but insoluble in ether. Yields vary from approximately 10 to 75%. Intrinsic viscosities (Table) in chloroform range from <0.1 to approximately 0.4 dl/g at 25°C.

The IR spectra (Note 6) show absorption bands in the following regions [cm-1]: 3000-2850 (CH stretch), 1730 (carbonyl stretch) and 1025 (ester C-O stretch). The 50 MHz $^{13}$C-NMR spectra have peaks for carbonyls at approximately 172 ppm, ether "-methylenes at approximately 70 ppm, methylenes " to the thioether at approximately 30-32 ppm, and backbone methine and methylene carbons at 27-45 ppm.

## 3. Notes

1. Caution. These operations should be carried out in a well-ventilated hood. Thiols are noxious materials.
2. Bis(2-alkoxycarbonyl-2-propenyl) ethers are obtained by DABCO catalyzed ether formation of alkyl "-(hydroxymethyl)acrylates (see accompanying procedures).
3. Dithiols are obtained from Aldrich Chemical, Fairfield Chemical or Parish Chemical and used without further purification.
4. Triethylamine is purified by distillation and stored over sieves.
5. A Bruker MSL-200 is employed to monitor the reaction. The checkers did not monitor the reaction in this way, and no monomer additions were made after the initial charging of the reaction vessel. Perhaps as a result, the checkers found yields and viscosities somewhat lower.
6. A Nicolet 5DX FTIR is used to obtain the infrared spectra.

## 4. Methods of Preparation

The Michael addition of thiols to double bonds leading to polymers is a well known reaction.[3] Attempts to prepare identical polymers using the method of Chiellini et al.,[4] were less successful, possibly due to chain termination because of moisture in the solvent. Our procedure works well for the ethyl ester diacrylate[5] (results in the Table) as well as for the methyl and butyl ester derivatives (results not given here). Liquid polysulfides are well known sealants having found use in the shipping, building, automotive and aerospace industries.[6]

**Components, Yields and Viscosities for Ethyl Ester Polymers**

| **RN** | **Yield** | **Viscosity** |
|---|---|---|
| $-CH_2-CH_2-$ | 9.7% | a |
| $-CH_2-CH_2-CH_2-$ | 33.7 | 0.27 |
| $-CH_2-CH_2-CH_2-CH_2-$ | 49.6 | 0.22 |
| $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$ | 16.9 | b |
| $-CH_2-CH_2-S-CH_2-CH_2-$ | 75.7 | 0.24 |
| $-CH_2-CH_2-O-CH_2-CH_2-$ | 64.9 | 0.40 |
| $-C_6H_4-O-C_6H_4-$ | 13.3 | a |

a: viscosity < 0.1
b: sample is insoluble in chloroform, DMSO and HFIP

## 5. References

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# A SIMPLE ONE-STEP SYNTHESIS OF UNSATURATED POLYESTERS

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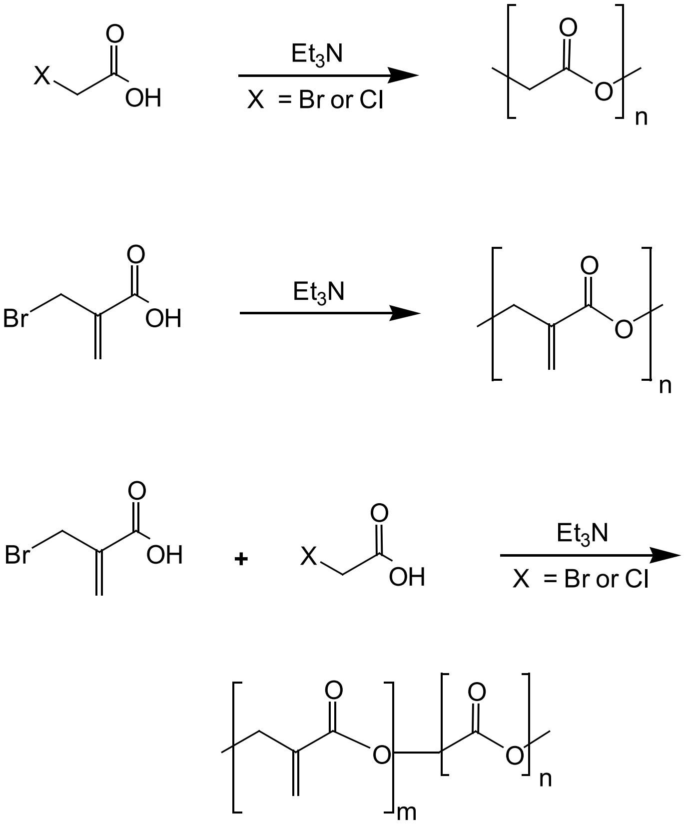
Checked by: A.G. Pinkus[2]



### 1. Procedure, Poly[oxy(1-oxo-1,2-ethanediyl)]

Chloroacetic acid (5.10 g, 54.0 mmol, Note 1) in refluxing anhydrous diethyl ether (30 ml) was treated with triethylamine (5.69 g, 56.4 mmol, Note 2) in diethyl ether (30 ml) and refluxed for 48 h. A precipitate is observed either upon addition of triethylamine or following formation of a two-phase system which gradually develops (according to the checkers). After cooling, the solid is filtered, washed repeatedly with ethanol and dried at approximately 100°C to give the product as a white powder. The yield is 2.1 g (67% of theoretical, Note 3).

### 2. Characterization, Poly[oxy(1-oxo-1,2-ethanediyl)]

Poly[oxy(1-oxo-1,2-ethanediyl)] is soluble in hexafluoroisopropyl alcohol (HFIP corrosive) and hot DMSO, and insoluble in most organic solvents. It has an intrinsic viscosity in HFIP at 25°C of 0.08 dl/g (Note 4) and shows a melting point of 214-219°C (lit.[3] mp 220-223°C, Note 5).

The IR spectrum (KBr pellet, Note 6) shows carbonyl absorptions at 1765 and 1749 $cm^{-1}$, CH deformation at 1439 and 1421 $cm^{-1}$, C-O stretch at 1236 and 1217 $cm^{-1}$ as well as other major absorptions at 1198, 1178 and 1095 $cm^{-1}$.

The 200 MHz $^1H$-NMR spectrum (Note 7) in HFIP at room temperature shows a single absorption at 4.91 ppm due to the aliphatic methylene.

Oligomer formation is confirmed by observation of multiple peaks in the 50 MHz $^{13}C$-NMR spectrum, taken in HFIP at room temperature, which shows carbonyl absorptions at 173.1 and 170.6 ppm and methylene absorptions at 63.5, 63.0 and 62.0 ppm. In DMSO-$d_6$ the carbonyls appear at 168.4 and 166.6 ppm and the methylenes at 61.1, 60.7, 59.9 and 59.2 ppm.

TGA thermograms (Note 8) show two main weight loss transitions, the first at 250°C and the second at 387°C due to catastrophic decomposition; residue at approximately 590°C is about 4.0%. A glass transition of 134°C and a melting transition of 205°C is determined by DSC.

## 3. Procedure, Poly("-oxymethylacrylate)

Triethylamine (3.27 g, 32.3 mmol) in chloroform (10 ml) is added dropwise to a solution of "-(bromomethyl)acrylic acid (4.21 g, 25.5 mmol, Note 9) and chloroform (50 ml), and the solution stirred at room temperature for 7 days. During this time a precipitate forms which is filtered, triturated with absolute ethanol (150 ml) to remove triethylammonium salts, dissolved in HFIP (the checkers suggest using nitromethane) and reprecipitated by addition to diethyl ether. The purification procedure is repeated twice and the product dried at 45°C for 18 h. The yield is 1.09 g (51.0% of theoretical, Note 10).

## 4. Characterization, Poly("-oxymethylacrylate)

Poly("-oxymethylacrylate) was found to be insoluble in all common organic solvents except HFIP. It has an intrinsic viscosity of 0.17 dl/g in HFIP at 25°C and displays a DSC melting point of 189-191°C (lit. mp[4] 194-254°C depending on molecular weight and thermal history).

The IR spectrum shows CH stretches at 3117, 3010 and 2951 cm$^{-1}$, a carbonyl stretch at 1723 cm$^{-1}$, a vinyl stretch at 1642 cm$^{-1}$, CH deformations at 1457, 1423, 1330, 1138, 1038 and 978 cm$^{-1}$, and other major absorbances at 1271, 825 and 653 cm$^{-1}$.

The 200 MHz $^{1}$H NMR spectrum in HFIP at room temperature shows vinyl peaks at 6.56 and 6.08 ppm and a methylene peak at 4.99 ppm. The 50 MHz $^{13}$C NMR spectrum in HFIP at room temperature shows a carbonyl peak at 168.7 ppm, vinyl carbons at 135.6 and 132.5 ppm, and a methylene peak at 65.3 ppm.

TGA thermograms show two predominate weight loss transitions at 380°C and 470°C with the latter involving catastrophic decomposition; residue at approximately 600°C varied from 4 to 15%. DSC shows a glass transition at 150°C, a melting exotherm at 192°C and an exothermic transition at 217°C presumed to be due to crosslinking followed by decomposition.

## 5. Procedure, Poly[oxy(1-oxo-1,2-ethanediyl)-co-("-oxymethylacrylate)][5]

Triethylamine (1.86 g, 18.4 mmol) in diethyl ether (30 ml, Note 11) is added dropwise to a refluxing solution of chloroacetic acid (830 mg, 8.9 mmol) and "-(bromomethyl)acrylic acid (1.42 g, 8.6 mmol) in diethyl ether (30 ml). Reflux is continued for 3 days giving a white precipitate. The precipitate is filtered, triturated with absolute ethanol (150 ml), air dried and further dried at 45°C under vacuum giving the product as a white powder. The yield is 0.71 g (58% of theoretical; the checkers report 71% yield).

## 6. Characterization, Poly[oxy(1-oxo-1,2-ethanediyl)-co-("-oxymethylacrylate)]

Copolymers containing high concentrations of acetate monomer are slightly soluble in DMSO; all copolymers are soluble in HFIP and insoluble in most other organic solvents. Most copolymers show intrinsic viscosities of less than 0.2 dl/g and melting transitions of approximately 180-187°C as determined by DSC.

The IR spectrum of a 1:1 copolymer shows absorptions at 3117, 3011 and 2957 cm$^{-1}$ attributed to CH stretches, a carbonyl stretch at 1716 cm$^{-1}$, a vinyl stretch at 1643 cm$^{-1}$, and other major peaks at 1457, 1337, 1144, 978 and 653 cm$^{-1}$.

The 200 MHz $^{1}$H NMR spectrum of a 1:1 copolymer in HFIP at room temperature displays vinyl protons at 6.66, 6.56, 6.15 and 6.07 ppm, and methylene absorbances at 4.99, 4.93 and 4.89 ppm. The 50 MHz $^{13}$C NMR spectrum of a 1:1 copolymer in HFIP at room temperature shows carbonyl peaks at 170.4 and 168.5 ppm, vinyl carbons at 135.6, 135.2, 133.4 and 132.4 ppm and methylene carbons at 66.4, 65.2 and 62.8 ppm.

TGA thermograms show transitions at about 230°C, 370°C, and 470°C involving catastrophic decomposition. Residual material at about 600°C varies from 2 to 16%. The copolymers show glass transitions of about 110 to 135°C as determined by DSC.

## 7. Notes

1. Haloacetic acids (chloro- and bromo-) are toxic and care should be employed in their use.
2. Triethylamine is distilled and stored over molecular sieves.
3. Triisooctylamine and refluxing ether gave only 6.9% yd.
4. A Cannon-Ubbelohde microviscometer is used.
5. A Leitz Orthoplan-Pol polarizing microscope equipped with a Mettler FD5 hot stage is used to obtain the melting points. The checkers indicate that the low melting point is probably due to residual ammonium salts that are difficult to remove. They report that dissolution in nitromethane, cooling and filtration eliminates this impurity.
6. A Nicolet 5DX FT-IR is used to obtain infrared spectra.
7. A Bruker MSL-200 NMR spectrometer is used.
8. A DuPont 9900 equipped with 910 DSC and 951 TGA modules is used to collect thermograms.
9. "-(Bromomethyl)acrylic acid may be purchased from Aldrich Chemical Company, purified by recrystallized from ethanol and stored in a desiccator. Care should be employed in its use as it is a toxic substance.
10. Successful polymerization of "-(bromomethyl)acrylic acid was also carried out in refluxing diethyl ether giving poly("-oxymethylacrylate) in 57% yield.
11. Chloroform, 2-nitropropane and nitromethane failed to yield any appreciable quantity of copolymer although the checkers indicate this is a good solvent for the homopolymerization.

## 8. Methods of Preparation

Polyglycolide, the simplest polyester, is a very important absorbable suture material. It has been successfully made by heating tartronic acid[6,7] or alkali salts of haloacetic acids;[8] by ring-opening polymerization of the six-membered ring glycolide;[9] and most recently by the reaction of haloacetic acids with tertiary amine bases.[3]

Poly("-oxymethylacrylate) has been previously prepared by the action of tertiary alkyl amines on "-(bromomethyl)acrylic acid,[4] and by the polyesterification of ethyl "-(hydroxymethyl)acrylate with tetrabutyltitanate.[10]

## 9. References

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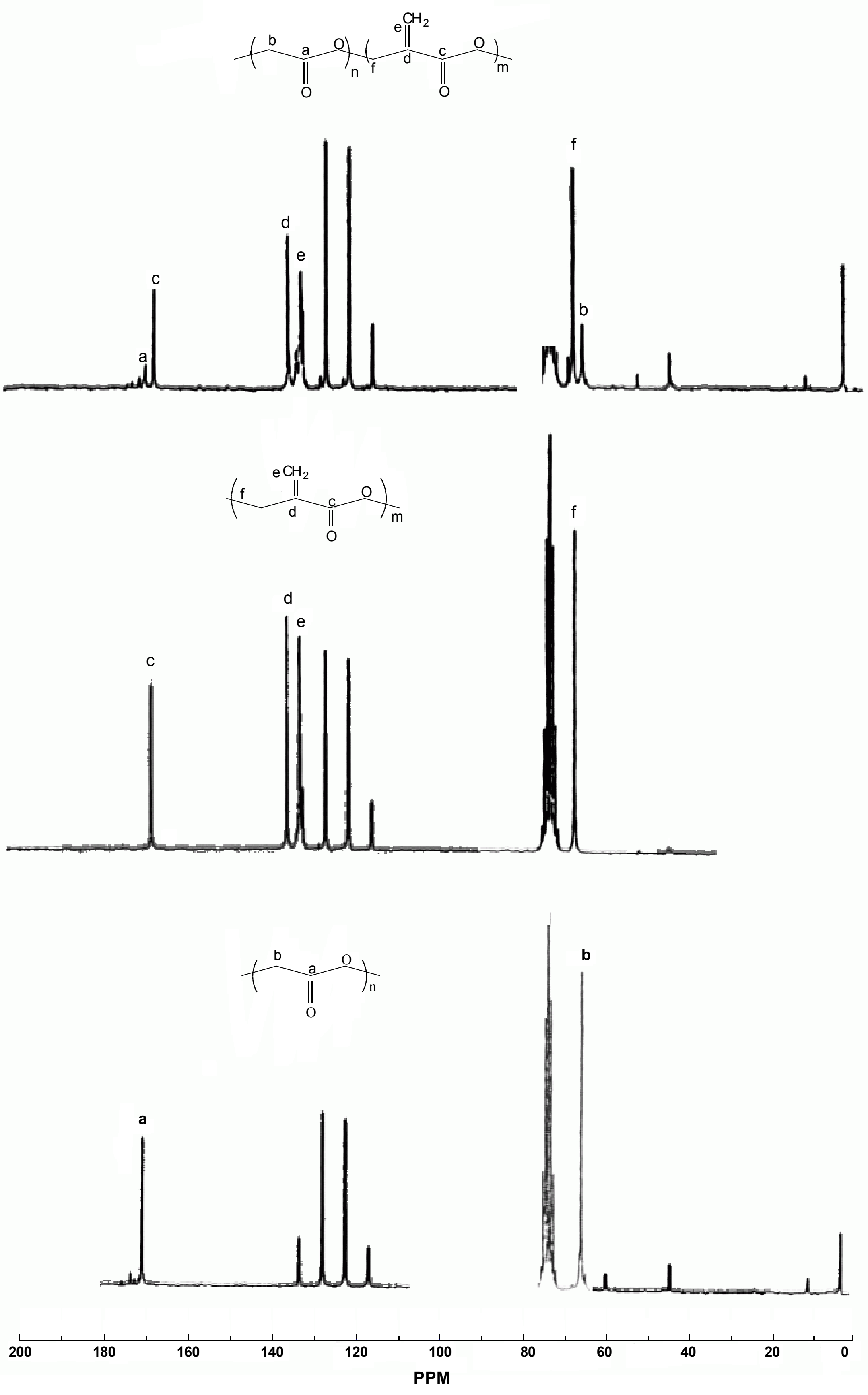
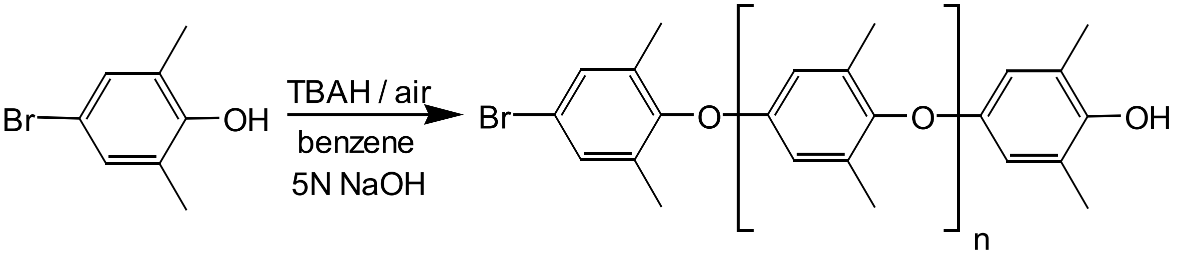


**$^{13}C$ Spectra in HFIP of polyglycolide (bottom trace), unsaturated homopolymer (middle) and 1:1 copolymer (top trace).**

# α-(4-BROMO-2,6-DIMETHYLPHENOXY)-ω-(3,5- DIMETHYL-4-HYDROXYPHENYL)-POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

**Virgil Percec and James H. Wang**[1]

Checked by: Jeno Muthiah and Lon J. Mathias[2]



## 1. Procedure

The polymerization of 4-bromo-2,6-dimethylphenol is carried out in an open, single-neck 1000 ml round-bottom flask (Note 1), equipped with an octagonal magnetic stirring bar (1 1/2" x 5/16" coated with Teflon, Fisher) on a stirring plate. 4-Bromo-2,6-dimethyl phenol (30 g, Note 2) is dissolved in 250 ml 6N aqueous NaOH. A yellow solution results after 5 min. Benzene (250 ml) and 2.53 g tetrabutylammonium hydrogen sulfate (TBAH, Note 3) are then added. The reaction mixture is stirred vigorously in the presence of air for 2.5 h (Note 4). The reaction mixture is then neutralized with excess (about 320 ml) 5N aqueous HCl. The benzene layer of the cooled reaction mixture is separated and poured into 2.5 l methanol yielding a white precipitate. The precipitate is filtered and dried in vacuo to yield poly(2,6-dimethyl-1,4-phenylene oxide) (yd 75 ± 5%).

## 2. Characterization

The resulting polymer is a white powder. The molecular weight and molecular weight distribution of the polymer are determined by size-exclusion chromatography (SEC, Note 5): $M_n = 7400 \pm 200$ g/mol, $M_w/M_n = 1.9 \pm 0.1$. The 200 MHz $^1$H NMR spectrum (Note 6) shows resonances at 2.08 (s,$C\underline{H}_3$ of the 2,6-dimethyl-1,4-phenylene unit), 3.97 (s, O$\underline{H}$ of the 3,5-dimethyl-4-hydroxyphenyl chain end), 6.24 (s, Ph-$\underline{H}$ of the 3,5-dimethyl-4-hydroxyphenyl chain end), 6.39 (s, Ph-$\underline{H}$ of the 2,6-dimethyl-1,4-phenylene repeating unit), 7.20 (s, Ph-$\underline{H}$ of the 4-bromo-2,6-dimethylphenoxy chain end). The glass transition temperature ($T_g$) of the polymer is 200 ± 5°C as determined by DSC (Note 7).

## 3. Significance

This synthesis produces PPO with one 4-bromo-2,6-dimethylphenoxy chain end and one 3,5-dimethyl-4-hydroxyphenyl chain end on each poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) macromolecule.[3] The functionality of the 2,6-dimethylphenol chain end is demonstrated by the phase transfer catalyzed etherification of the phenol group with *p*-chloromethylstyrene.[4] This etherification results in a vinylbenzyl ether macromonomer of PPO and this technique will be described in an accompanying procedure. PPO can also be synthesized by polymerization of 2,6-dimethylphenol catalyzed by a copper-amine complex[5] or in a two-phase polymerization of 4-bromo-2,6-dimethylphenol in the presence of an oxidant.[6]

## 4. Notes

1. The reaction can also be performed in a 1000 ml Erlenmeyer flask or 1 l beaker capable of allowing excellent stirring.
2. 4-Bromo-2,6-dimethylphenol (97%, Aldrich) is recrystallized from petroleum ether, mp 78-79°C. The polymerization can also be carried in smaller or larger quantity than 30 g of 4-bromo-2,6-dimethylphenol as long as good stirring can be maintained.
3. Tetrabutylammonium hydrogen sulfate (TBAH, 97%, Aldrich) phase transfer catalyst is used as received.

4. The molecular weight and yield depend on the polymerization time.[4] Shorter time results in lower yield and lower molecular weight. The checkers extended the reaction to 3.5 h, and obtained polymer with $M_n$ of 23,000 by SEC.
5. SEC measurements are performed on a Perkin-Elmer series 10LC instrument equipped with an LC-100 column oven, an LC-600 auto sampler, and a Nelson Analytical 900 series data station. The measurements are made using a UV detector set at 254 nm with chloroform as solvent (1 ml/min), a set of PL-gel columns (500 and $10^4$Å), and a calibration plot constructed with polystyrene standards (Supelco).
6. 200 MHz $^1$H NMR spectra are recorded on a Varian XL-200 spectrometer. The spectra are recorded in $CCl_4$ with TMS as the internal standard using a delay between transients of 2 s and an acquisition time of 2 s. The checkers also analyzed the polymer by $^{13}$C NMR of a $CDCl_3$ solution. Figure 1 gives the spectrum. The assignments of both $^1$H and $^{13}$C NMR spectra are described elsewhere.[7]
7. DSC analyses are performed with a Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, at a heating rate of 20°C/min. The instrument is calibrated with an indium standard. The glass transition temperature ($T_g$) is read at the middle of the change in the heat capacity during the second heating scan.

## 5. References

1. Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106.
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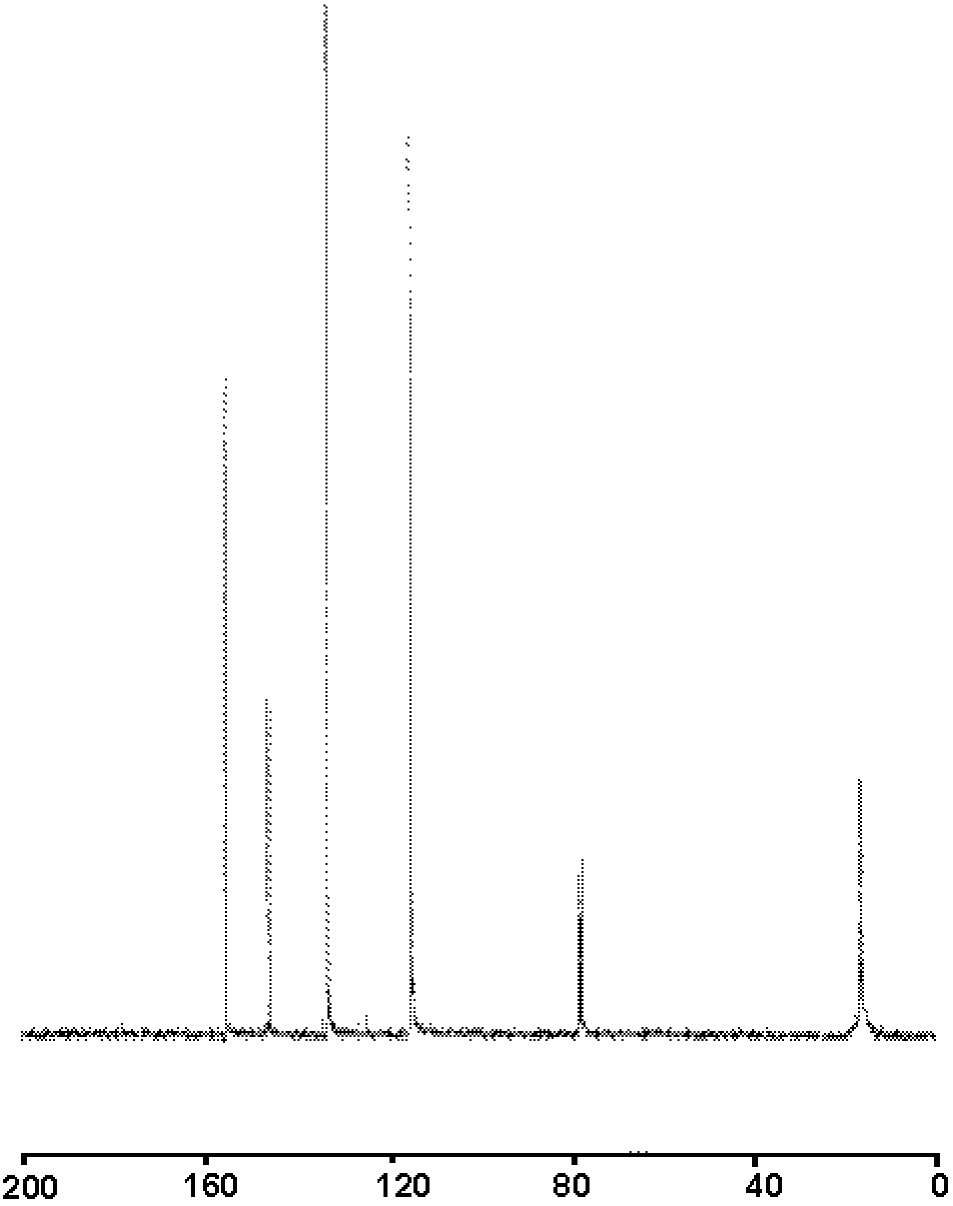
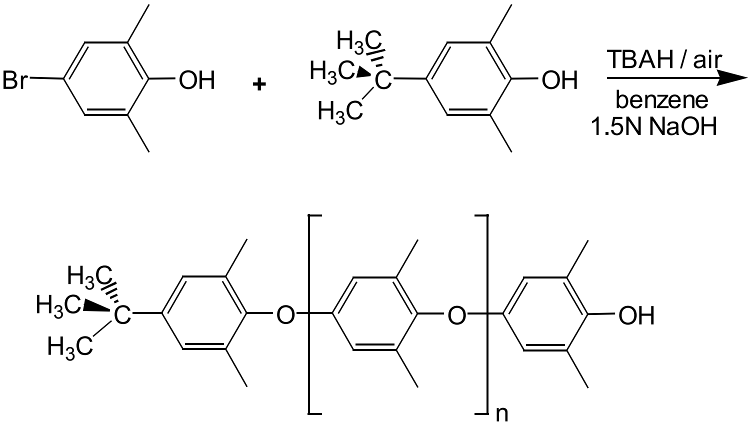


**Figure 1.** $^{13}$C NMR spectrum in $CDCl_3$ of a-(4-bromo-2,6-dimethyl-phenoxy-w-(3,5-dimethyl-4-hydroxyphenyl)-poly(2,6-dimethyl-1,4-phenylene oxide).

# "-(4-TERT-BUTYL-2,6-DIMETHYLPHENOXY)- *T*-(3,5-DIMETHYL-4-HYDROXYPHENYL)-POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

**Virgil Percec and James H. Wang**[1]

Checked by: Jeno Muthiah and Lon J. Mathias[2]



## 1. Procedure

The title polymer is synthesized by a phase transfer catalyzed (PTC) copolymerization of 4-bromo-2,6-dimethylphenol with 4-*tert*-butyl-2,6-dimethylphenol. The polymerization is performed in an open single-neck 250 ml round-bottom flask (Note 1), equipped with an octagonal magnetic stirring bar (1 1/2" x 5/16" coated with Teflon, Fisher) on a stirring plate. 4-*tert*-butyl-2,6-dimethylphenol[3] (0.44 g, Note 2) is dissolved in 50 ml 1.5N aqueous NaOH under stirring at room temperature. 4-Bromo-2,6-dimethyl phenol (5.00 g, Note 3) is subsequently dissolved in the reaction flask. Benzene (30 ml) and 0.476 g tetrabutylammonium hydrogen sulfate (TBAH, Note 4) are then added. The reaction mixture is stirred vigorously at room temperature in the presence of air for 13 h (Note 5). Excess 1.5N aqueous hydrochloric acid (55 ml) is added to the flask under vigorous stirring. The benzene layer of the cooled mixture is separated and poured into 500 ml methanol. The precipitate is filtered, washed with 200 ml methanol, and dried *in vacuo* to give "-(4-*tert*-butyl-2,6-dimethylphenoxy)-T-(3,5-dimethyl-4-hydroxyphenyl)-poly(2,6-dimethyl-1,4-phenylene oxide) (yd 35 ± 5%).

## 2. Characterization

The dried polymer is obtained as a white powder. The molecular weight and molecular weight distribution of the polymer are determined by size-exclusion chromatography (SEC, Note 6): $M_n$ = 2400 ± 200 g/mol, $M_w/M_n$ = 1.2 ± 0.1. ($M_n$ of 2500 g/mol was obtained by the checkers with 42% yd.) The 200 MHz $^1$H NMR spectrum (Note 7) exhibits resonances at 1.33 [s, $-C(C\underline{H}_3)_3$ of the 4-*tert*-butyl-2,6-dimethylphenoxy chain end], 2.09 (s, $C\underline{H}_3$ of the 2,6-dimethyl-1,4-phenylene unit), 3.99 (s, O$\underline{H}$ of the 3,5-dimethyl-4-hydroxyphenyl chain end), 6.24 (s, Ph-$\underline{H}$ of the 3,5-dimethyl-4-hydroxyphenyl chain end), 6.39 (s, Ph-$\underline{H}$ of the 2,6-dimethyl-1,4-phenylene repeating unit), 7.00 (s, Ph-$\underline{H}$ of the 4-*tert*-butyl-2,6-dimethylphenoxy chain end) (Notes 8 and 9). The glass transition temperature ($T_g$) of the polymer is 150 ± 5$^o$C as determined by DSC (Note 10).

## 3. Significance

The phase transfer catalyzed (PTC) homopolymerization of 4-bromo-2,6-dimethylphenol produces poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with one 3,5-dimethyl-4-hydroxyphenyl chain end/PPO molecule (PPO-OH).[4] However, the polydispersities of the resulting PPO-OH are high and tedious fractionation is usually required for macromonomer applications.[5] The molecular weight of the resulting PPO-OH can only be controlled by stopping the polymerization at very low conversions (typically <10%).[4] This PTC copolymerization procedure leads to PPO-OH of narrow polydispersities (<1.40) at relatively high polymer yield (up to 74%).[6] The molecular weight of the resulting PPO-OH can be conveniently controlled by the molar ratio of the 4-bromo-2,6-dimethylphenol to 4-*tert*-butyl-2,6-dimethylphenol in the initial monomer mixture.[6] PPO can also be synthesized by alternative polymerization of 2,6-dimethylphenol catalyzed by copper-amine complex[7] or by a two-phase polymerization of 4-bromo-2,6-dimethylphenol in the presence of an oxidant.[8] PPO with narrow molecular weight distribution was previously prepared by complexation of PPO oligomers with $CH_2Cl_2$ or $CH_2Br_2$.[9]

## 4. Notes

1. The polymerization can also be carried out in a 250 ml Erlenmeyer flask or beaker capable of allowing excellent stirring.
2. 4-*tert*-Butyl-2,6-dimethylphenol is synthesized by a modification of a literature procedure.[3] $H_2SO_4$ (72%, 236 g) is added dropwise to a mixture of 2,6-dimethylphenol (71 g, 0.58 mol) and *t*-butanol (72 g, 0.72 mol), and the reaction is stirred at 60°C for 4 h. Three portions of diethyl ether are used to extract the reaction mixture. The ether extracts are then washed with saturated $NaHCO_3$ and water, and dried with anhydrous $CaCl_2$. Ether is removed on a rotary evaporator. The residue is recrystallized from petroleum ether to yield white crystals (70 g, 68%); mp 78-80°C (lit. mp 81-82°C); purity >99% by HPLC (Note 11).[6] $^1$H NMR ($CDCl_3$, TMS, 25°C): 1.28 [s, 9H, $\text{-C(C}\underline{\text{H}}_3)_3$], 2.25 (s, 6H, $\text{Ph-C}\underline{\text{H}}_3$), 4.46 (s, 1H, $\text{Ph-O}\underline{\text{H}}$), 7.00 (s, 2H, $\text{Ph-}\underline{\text{H}}$). Less 4-*tert*-butyl-2,6-dimethylphenol than 0.44 g will lead to PPO-OH of higher molecular weight.[6] The reaction yields a crude product of 91% as analyzed by the checkers using gas chromatography.
3. 4-Bromo-2,6-dimethylphenol (97%, Aldrich) is recrystallized from petroleum ether; mp 78-79°C.
4. Tetrabutylammonium hydrogen sulfate (TBAH, 97%, Aldrich) phase transfer catalyst is used as received.
5. Longer reaction time results in higher polymer yield. A detailed study of the influence of polymerization time on both the yield and the molecular weight of the polymer has been described in detail.[6]
6. SEC measurements are performed on a Perkin-Elmer series 10LC instrument equipped with an LC-100 column oven, an LC-600 autosampler, and a Nelson Analytical 900 series data station. The measurements are made using a UV detector set at 254 nm, chloroform as solvent (1 ml/min), a set of PL-gel columns (500 and $10^4$Å), and a calibration plot constructed with polystyrene standards (Supelco).
7. 200 MHz $^1$H NMR spectra are recorded on a Varian XL-200 spectrometer. The spectra are recorded in $CCl_4$ with TMS as the internal standard using a delay between transients of 2 s and an acquisition time of 2 s.
8. The checkers confirmed incorporation of the "-4-*tert*-butyl-2,6-dimethyl phenoxy group by $^{13}$C NMR (Figure 1) which shows the *tert*-butyl methyl groups at 31.5 ppm and the quaternary carbon at 34.2 ppm.
9. The PPO-OH synthesized at high molar ratio of 4-bromo-2,6-dimethylphenol to 4-*tert*-butyl-2,6-dimethylphenol also exhibits a resonance due to 4-bromo-2,6-dimethylphenoxy chain end.[6]
10. DSC analyses are performed with a Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, at a heating rate of 20°C/min. The instrument is calibrated with an indium standard. The glass transition temperature ($T_g$) is read at the middle of the change in the heat capacity during the second heating scan. The $T_g$ value varies strongly with the molecular weight of the polymer.
11. HPLC analyses are made on the same instrument (Note 6) on a 100Å PL-gel column using chloroform as eluent (1.0 ml/min).

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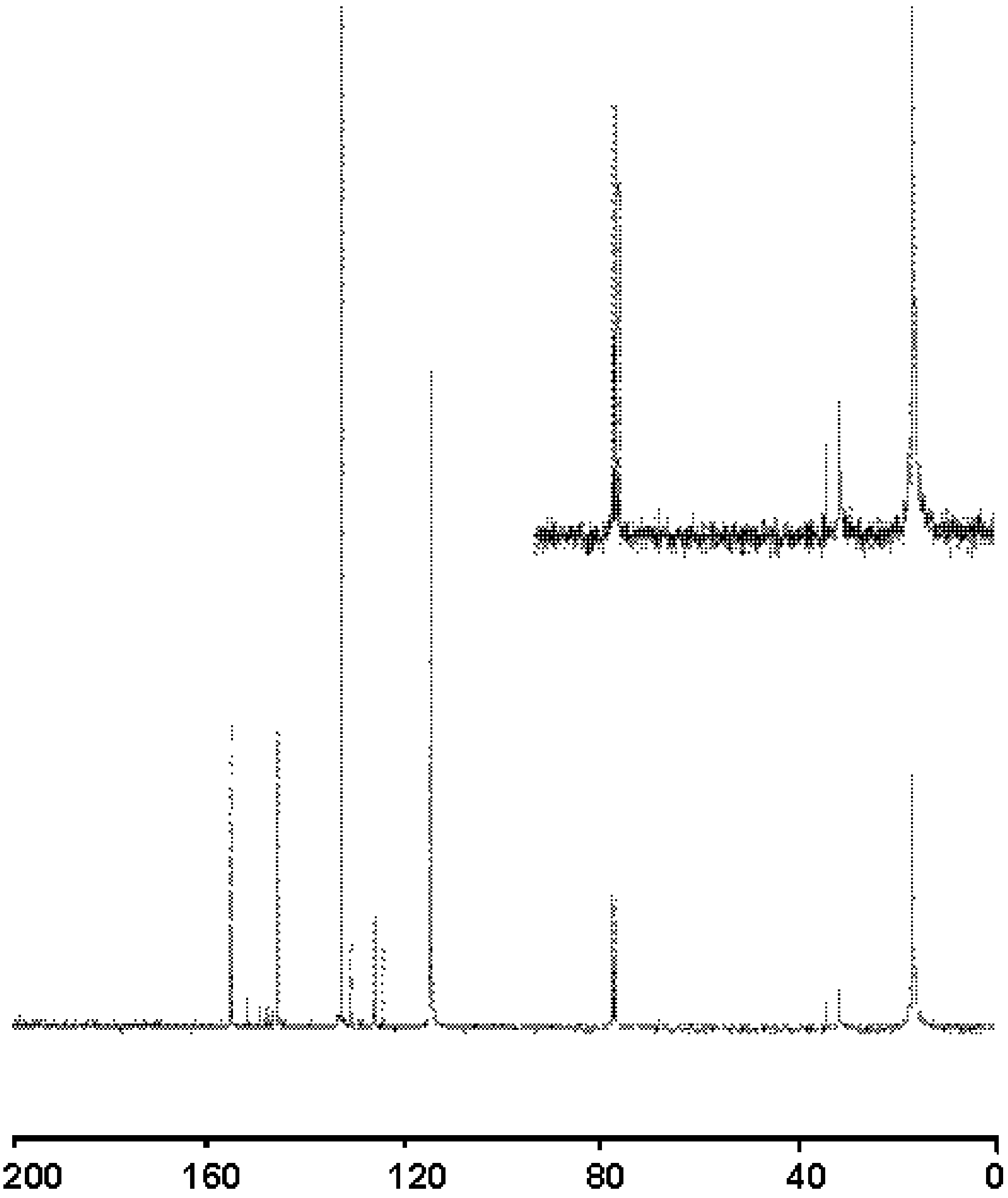

**Figure 1.** $^{13}C$ NMR spectrum in $CDCl_3$ of α-4-tert-butyl-2,6-dimethyl-phenoxy-ω-(3,5-dimethyl-4-hydroxyphenyl)-poly(2,6-dimethyl-1,4-phenylene oxide).

# *T*-(Vinylbenzyl Ether) Macromonomer of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)

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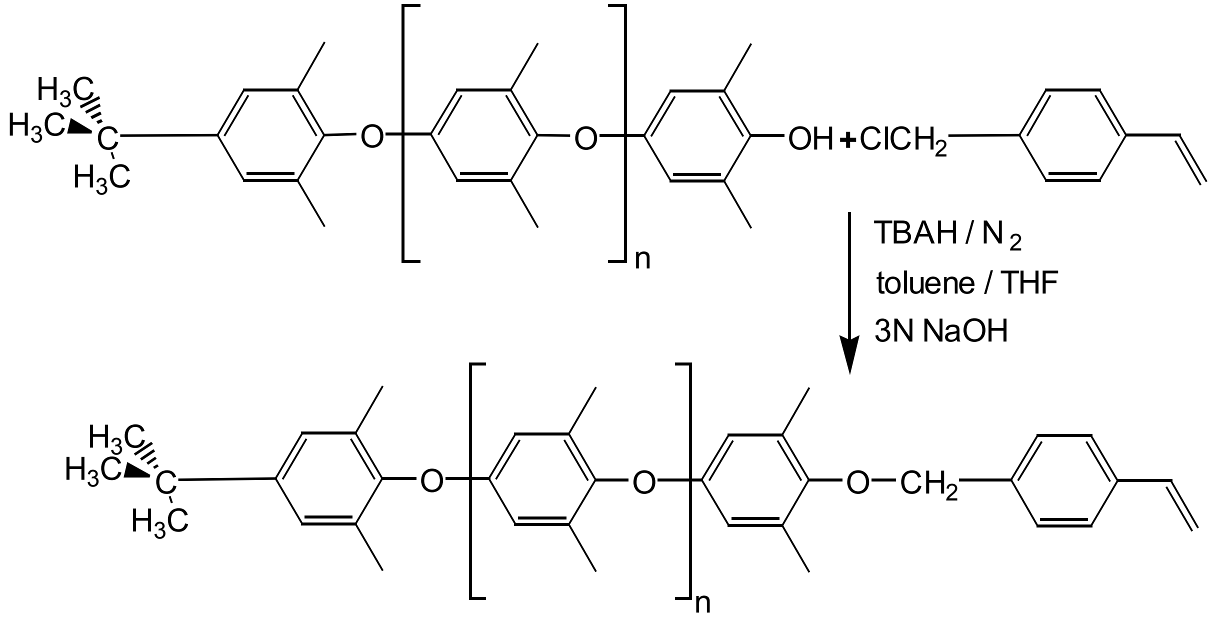
Checked by: Jeno Muthiah and Lon J. Mathias[2]



## 1. Procedure

In a 25 ml single-neck round-bottom flask (Note 1), equipped with an octagonal magnetic stirring bar (1/2" x 3/16" coated with Teflon, Fisher), "-(4-*tert*-butyl-2,6-dimethylphenoxy)-T-(3,5-dimethyl-4-hydroxyphenyl)-poly(2,6-dimethyl-1,4-phenylene oxide)[3] (PPO-OH, $M_n$ = 2400 ± 100 g/mol, $M_w/M_n$ = 1.25 ± 0.01, 0.5 g, Note 2) is dissolved in 5 ml toluene (Note 3), and subsequently 5 ml tetrahydrofuran is added. The flask is fitted with a septum-$N_2$ inlet-outlet assembly (Note 4). $N_2$ is bubbled into the solution for 1 h to remove dissolved air. Deaerated *p*-chloromethylstyrene (0.5 g, Note 5) and 2 ml deaerated 3N aqueous NaOH are then added, and the contents of the flask are deaerated for 1 h by bubbling $N_2$. Finally, 70 mg TBAH (Note 6) is added. The reaction mixture is stirred vigorously at room temperature under $N_2$ for 14 h (Note 7). At the end of the reaction, the reaction mixture is neutralized with 5 ml 1.5N hydrochloric acid. The benzene layer (top layer) of the cooled reaction mixture is separated in a separatory funnel and subsequently poured into 150 ml methanol. The resulting precipitate is washed with 60 ml methanol and dried *in vacuo*. The dried polymer is then dissolved in 5 ml chloroform and precipitated into 75 ml methanol. The precipitate is filtered and dried *in vacuo* to give the title macromonomer; crude yd - 100%. Due to fractionation during precipitation into methanol (low molecular weight PPO is soluble in methanol[3,4]), the isolated yield of the macromonomer is 90 ± 5%.

## 2. Characterization

The obtained macromonomer is a white powder. The molecular weight and molecular weight distribution of the polymer are determined by SEC (Note 8): $M_n$ = 3200 ± 200 g/mol, $M_w/M_n$ = 1.25 ± 0.05 (Note 9). The 200 MHz $^1H$ NMR spectrum (Note 10) exhibits peaks at 1.33 (s, $-C(C\underline{H}_3)_3$ of the 4-*tert*-butyl-2,6-dimethylphenoxy chain end), 2.09 (s, $C\underline{H}_3$ of the 2,6-dimethyl-1,4-phenylene unit), 4.71 (s, $-OC\underline{H}_2$), 5.19 (d, $\underline{H}CH$ = CH-), 5.68 (s, $\underline{H}CH$=CH-), 6.27 (s, Ph-$\underline{H}$ of the 2,6-dimethyl-1,4-phenylene group next to the vinyl benzyl ether chain end), 6.38 (s, Ph-$\underline{H}$ of the 2,6-dimethyl-1,4-phenylene repeating unit), 6.58-6.73 (dd, $CH_2 = C\underline{H}$-), 6.99 (s, Ph-$\underline{H}$ of the 4-*tert*-butyl-2,6-dimethylphenoxy chain end), 7.32 (s, Ph-$\underline{H}$ of the vinylbenzyl ether group). Within experimental error, the integral of the resonance at 7.32 is twice that at 6.99. This demonstrates that the T-(vinylbenzyl ether) macromonomer of poly(2,6-dimethyl-1,4-phenylene oxide) synthesized by this method is monofunctional.

Additional support for monofunctionality comes from the fact that it can be incorporated completely into a graft copolymer by radical copolymerization with methyl methacrylate.[5] The $^{13}C$ NMR spectrum obtained by the checkers confirms the presence of the vinyl benzyl -$CH_2$-O- group at 73.9 ppm as shown in Figure 2.

## 3. Significance

The phase transfer catalyzed etherification of the T-(3,5-dimethyl-4-hydroxyphenyl) chain end of poly(2,6-dimethyl-1,4-phenylene oxide) leads to the vinylbenzyl ether macromonomer of PPO (PPO-VBE).[5,6] The functionality of the macromonomer is demonstrated by its 200 MHz $^1H$ NMR spectrum (c.f. Characterization),[3,5,] and by the free radical copolymerization of the PPO-VBE macromonomer with methyl methacrylate and *n*-butyl methacrylate whence it is completely incorporated into the graft copolymer.[5] These copolymerizations produce soluble graft copolymers which indirectly confirm that each macromonomer molecule contains only one T-(vinylbenzyl ether) group (i.e. is monofunctional).[5,6,7]

## 4. Notes

1. The reaction can also be carried out in a 25 ml Erlenmeyer flask which provides a good fit with the septum assembly (Note 4).
2. The PPO-OH was synthesized by the phase transfer catalyzed copolymerization of 4-bromo-2,6-dimethylphenol with 4-*tert*-butyl-2,6-dimethylphenol[3]; SEC measurement (Note 8) gives $M_n$ = 2400 ± 100 g/mol, $M_w/M_n$ = 1.21 ± 0.01. PPO-OH of other molecular weight can be functionalized with this procedure by adjusting the stoichiometry according to the molecular weight of the sample.
3. Toluene and all other solvents (Fisher) are used as received.
4. The flask is fitted with a septum. A long needle (18") is inserted through the septum with the needle tip below the solution and the other end connected to a $N_2$-inlet. A short needle is inserted into the septum to lead the $N_2$-outlet to a bubbler (Figure 1).
5. *p*-Chloromethylstyrene (Seimi Chemical, Kanagawa, Japan) is used as received. The checkers used a mixture of *m*- and *p*-chloromethylstyrene available from Aldrich or Polysciences. The synthesis of *p*-chloromethylstyrene is also available in the literature.[8]
6. Tetrabutylammonium hydrogen sulfate (TBAH, 97%, Aldrich) phase transfer catalyst is used as received.
7. If this reaction is performed in the presence of air, a radical-anion redistribution of PPO competes with the $S_N2$ etherification of the polymer chain end and will give rise to polymer with completely different molecular weight and molecular weight distribution.[9,10]
8. SEC measurements are performed on a Perkin-Elmer series 10LC instrument equipped with an LC-100 column oven, an LC-600 autosampler, and a Nelson Analytical 900 series data station. The measurements are made using a UV detector set at 254 nm, chloroform as solvent (1 ml/min), a set of PL-gel columns (500 and $10^4$Å), and a calibration plot constructed with polystyrene standards (Supelco).
9. The increase of the molecular weight from 2400 ± 100 g/mol to 3200 ± 200 g/mol is due to the fractionation of the low molecular weight macromonomer during precipitation into methanol.[3,4] Low molecular weight PPO (<800 g/mol) and its macromonomer are soluble in methanol. When higher molecular weight starting PPO-OH is used, the molecular weight change after the etherification is less important.
10. 200 MHz $^1H$ NMR spectra are recorded on a Varian XL-200 spectrometer using $CCl_4$ solvent with TMS as the internal standard. The spectra were recorded with a delay between transients of 2 s and an acquisition time of 2 s. The assignments of both $^1H$ and $^{13}C$ NMR spectra are described elsewhere.[11]

## 5. References

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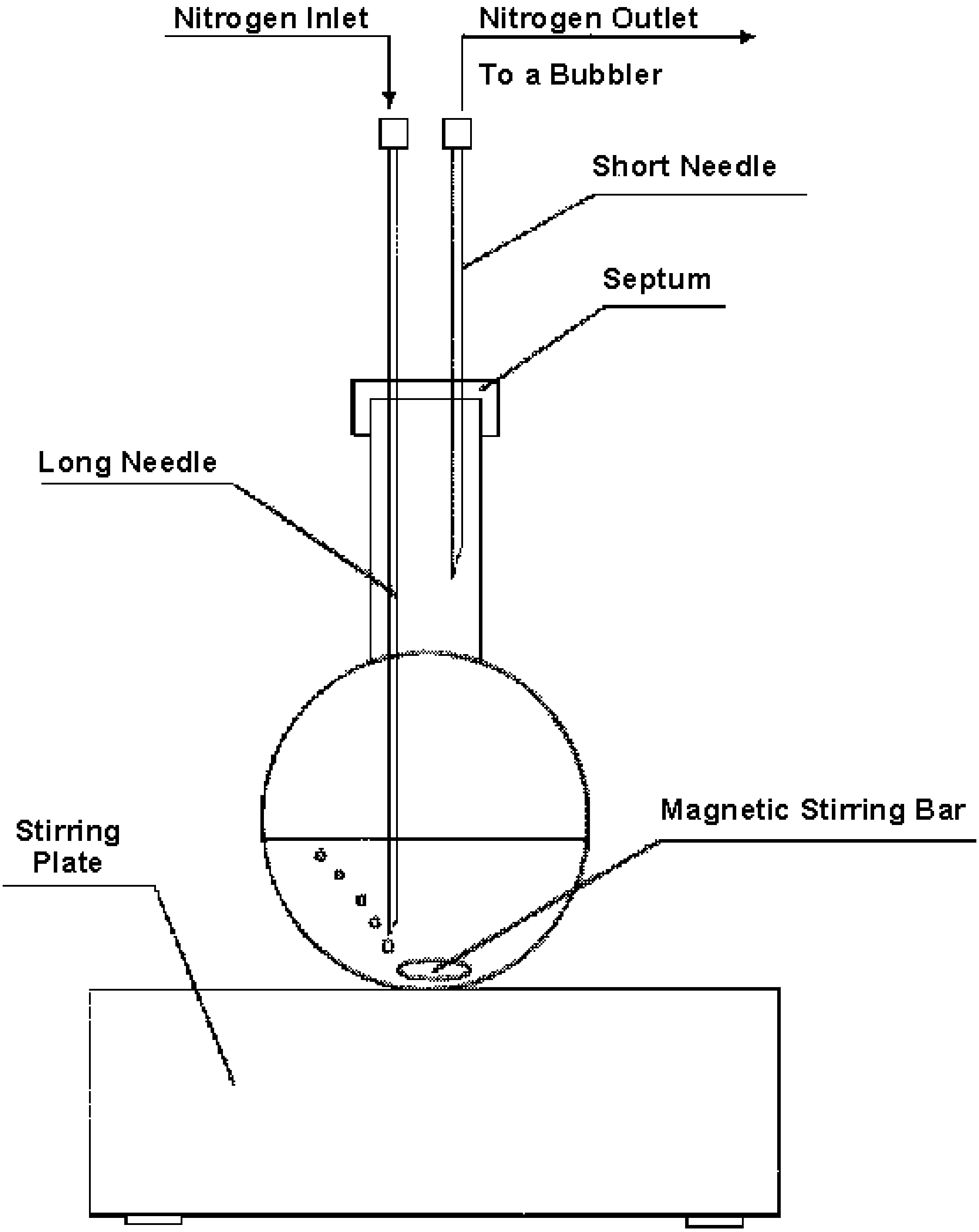

**Figure 1. Septum-equipped reaction flask for polymer.**

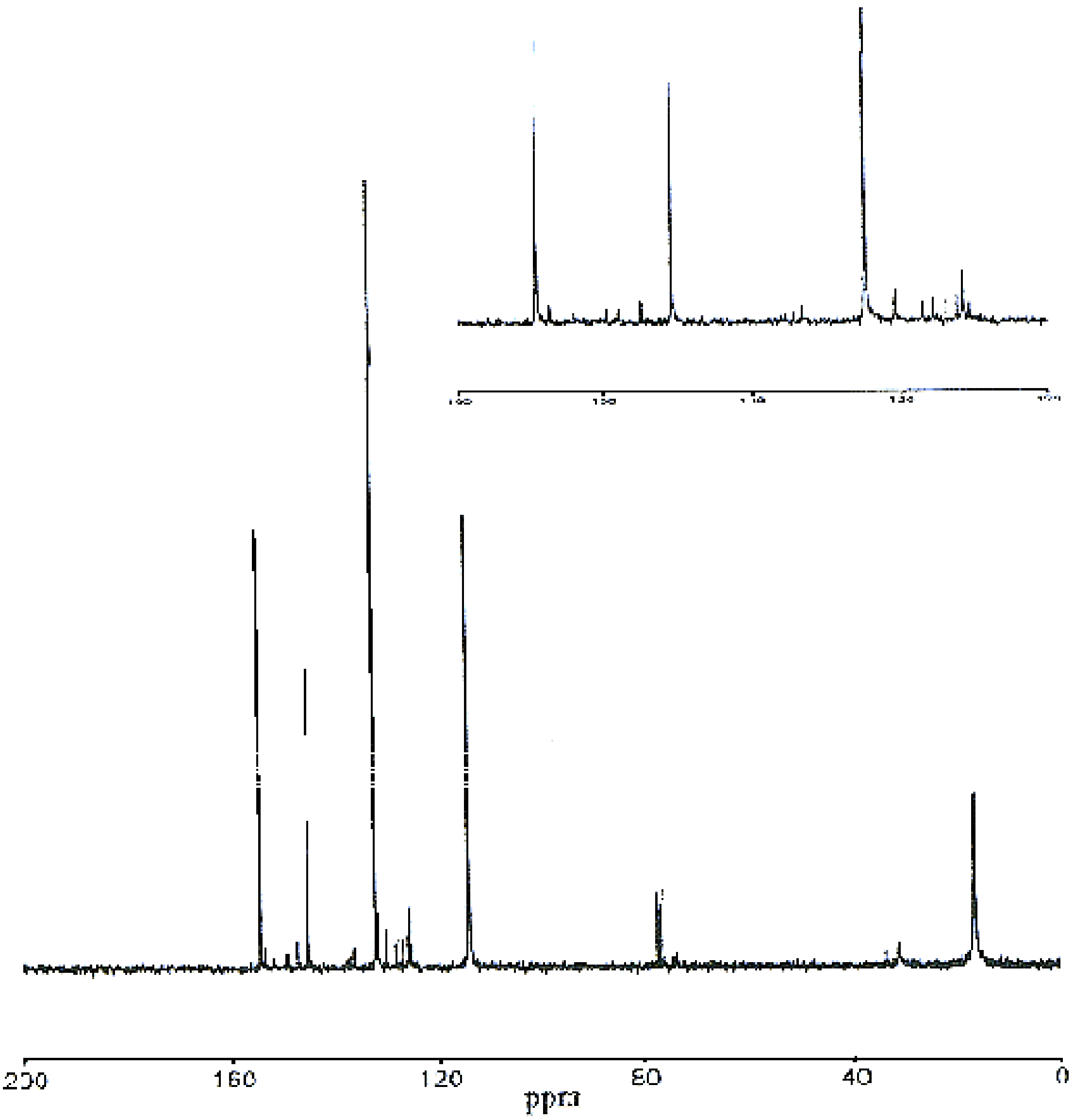

**Figure 2. $^{13}$C spectrum in $CDCl_3$ of the macromonomer of poly(2,6-dimethyl-1,4-phenylene oxide).**