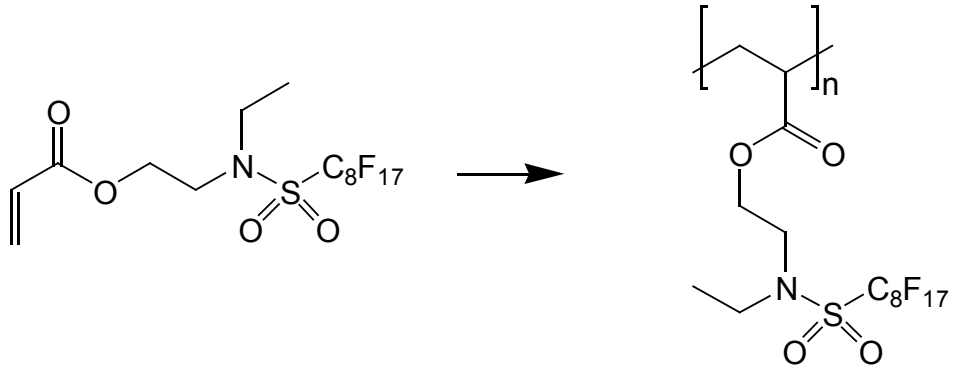
POLY(N- ETHYL PERFLUOROOCTANE SULPHONAMIDO ETHYL ACRYLATE)

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°C. The checkers recrystallized twice from methanol alone to a melting point of 42.5-43.5°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.

4. References

1. Current Address: Polaroid Corporation, 730 Main Street, Cambridge, MA 02139. The work was done at the 3M Company in St. Paul, MN.
2. Corporate Polymer Research Department, S.C. Johnson and Son, Inc., Racine, WI 53403.
3. R. Ramharack and T. H. Nguyen, *J. Polym. Sci.: Part C: Polym. Lett.* , 25, 93 (1987).
4. R. Ramharack, *Polym. Prpts Am. Chem. Soc.*, 29(1), 146 (June 1988), ACS 198th meeting in Toronto.