Polymer Bulletin 13, 337-342 (1985)

Polymer Bulletin

Polymerization of Epoxides and Vinyl Monomers by Nitrosyl Hexafluorophosphate

S. L. N. Seung[a], P. Dreyfuss[a], and L. J. Fetters[b]

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, USA

Summary

The polymerization of certain 1,2-epoxides, styrene and n-butyl vinyl ether has been accomplished by the use of nitrosyl hexafluorophosphate as the initiator. Heretofor, nitrosyl hexafluorophosphate has been known as an initiator only for tetrahydrofuran. The polymers prepared had broad molecular weight distributions.

Nitrosyl hexafluorophosphate ($NOPF_6$) has been used to initiate the polymerization of tetrahydrofuran (ECKSTEIN and DREYFUSS, 1979; SEUNG, et. al., 1981). In this communication we report on the use of $NOPF_6$ for the polymerization of three 1,2-epoxides, namely styrene oxide (SO), cyclohexene oxide (CHO), and 1,2-epoxybutane (EB). In addition, styrene (S) and n-butyl vinyl ether (nBVE) were also polymerized with this initiator.

Experimental

The Hewlett-Packard 503 osmometer (with an S and S - 08 membrane) was used to determine the number-average molecular weights. Measurements were made with toluene solutions at 37°C. The molecular weights were calculated from the usual $(\pi/c)^{\frac{1}{2}}$ vs. c plots.

Gel permeation chromatograms were run on a Waters 150 C chromatograph with six 30-cm·μ-Styragel columns (10^6, 10^5, 10^4, 10^3, $5\mathrm{x}10^2$ and 10^2 Å) equipped with a differential refractometer. Tetrahydrofuran was the carrier solvent and solution concentrations were ¼% (w/v). A 1 ml min^{-1} flow rate was used while the column temperature was 35°C.

The high-vacuum line technique (MORTON and FETTERS, 1975) was employed for the polymerization. The epoxide monomers (Aldrich Chemical Co.) were stirred over calcium hydride for at least one day with occasional degassing. They then were distilled into graduated

---

[a] Present address: Michigan Molecular Institute, Midland, Michigan 48640, USA

[b] Present address: Exxon Research and Engineering Co., Corporate Research, Science Laboratories, Clinton Township, Rt. 22 East, Annandale, New Jersey 08801, USA

ampoules fitted with break seals. Styrene (Fisher) was first dried over calcium hydride, then it was distilled into a flask containing dibutyl magnesium (Lithco). The mixture was stirred for a few hours by which time it had turned yellow. The styrene was then distilled into a similar ampoule. nBVE (Aldrich) was washed five times with dilute aqueous sodium hydroxide, then it was dried over sodium hydroxide pellets, and finally over calcium hydride overnight. It was then transferred into a flask containing calcium hydride and the mixture was stirred on the high-vacuum line for a few hours. Then the nBVE was distilled into a graduated ampoule fitted with a break seal. The polymerization reactor was a 200 ml flask which had a ground glass joint and a side arm to which the ampoule containing the monomer was attached. The reactor was attached to the vacuum line through the ground glass joint and was heated with a light flame so as to remove residual moisture. After a good vacuum had been established, the reactor was removed from the vacuum line, flushed with argon, and the $NOPF_6$ initiator was added. The reactor was then reattached to the vacuum line. After the reactor was evacuated, it was sealed off from the vacuum line. The monomer was then introduced into the reactor by rupturing the break seal with a glass-coated magnet. Methanol was used to terminate the polymerization reaction.

Preparation of Poly(SO): SO (46.2g, 0.38 mole) was added to the $NOPF_6$ (0.07 g, 0.4 m mole) in the evacuated reactor at 0°C. On addition, a light yellow precipitate was formed and the mixture was stirred at 0°C for 48 hrs., by which time it had turned slightly viscous. The polymerization was terminated and the mixture was dissolved in tetrahydrofuran, filtered and precipitated with methanol. After drying in a vacuum oven, the yield of the white powder was 3.6 g.

Preparation of Poly(CHO): CHO (37.8 g, 0.38 mole) was added to the $NOPF_6$ (0.07 g, 0.4 m mole) in the evacuated reactor at 0°C. Initially, some white precipitate was formed, and on stirring for about 2 hrs., it dissolved to give a colorless solution. This solution was kept at 0°C for 48 hrs. before termination. The mixture was dissolved in tetrahydrofuran, filtered and precipitated with methanol. A white powder was obtained and dried in a vacuum oven; yield, 4.2 g.

Preparation of Poly(EB): On addition of EB (27.3 g, 0.38 mole) to $NOPF_6$ (0.07 g, 0.4 m mole) at 0°C, some colorless gas was evolved and the $NOPF_6$ dissolved to give a colorless solution. The reaction was fairly exothermic. The reaction solution was stirred at 0°C and after ten minutes, it turned slightly viscous. After maintaining the polymerizing mixture at 0°C for

24 hrs., methanol was added. This mixture was added to tetrahydrofuran, filtered and precipitated with ice-water. A colorless gum was obtained and after vacuum drying, the yield was 18.3 g.

Preparation of Poly(S): When S (40.0 g, 0.38 mole) was added to $NOPF_6$ (0.07 g, 0.4 m mole) at 0°C, a light yellow precipitate was formed. This reaction mixture was stirred at 0°C for 48 hrs., then methanol was added to the light yellow viscous solution to terminate the polymerization. The mixture was dissolved in tetrahydrofuran, filtered and precipitated with methanol. The white powdery product was dried in a vacuum oven and the yield was 7.2 g.

Preparation of Poly(nBVE): nBVE (38.5 g, 0.38 mole) was added to $NOPF_6$ (0.07 g, 0.4 m mole) at 0°C with stirring. On addition, some brown precipitate was formed and the mixture turned slightly viscous after ten minutes. The mixture was kept at 0°C for 8 hrs., then the reaction was terminated. This mixture was dissolved in tetrahydrofuran, filtered, and on precipitation with ice water, a light yellow gum was obtained. After vacuum drying, the yield of this gum was 36.5 g.

Results and Discussion

There is, to date, no information on the polymerizations of epoxide or vinyl monomers by $NOPF_6$. However, nitrosyl hexafluoroantimonate has been reported as an initiator for the polymerization of a number of epoxides and cyclic ethers (BRITISH INDUSTRIAL PLASTICS, LTD., 1966) while dinitrosyl iron complexes are reported to initiate the polymerization of styrene, isobutene and tetrahydrofuran (BALLIVET-TKATCHENKO, et.al., 1981).

Table I contains our findings regarding the polymerization yields, number-average molecular weights, and heterogeneity indices of the polymers prepared using $NOPF_6$. Therein, it can be seen that under the reaction conditions chosen, the reactivity of the monomers increases in the order SO<CHO<S<EB<nBVE.

With the exception of EB, the molecular weights of the polymers were larger than the corresponding calculated values (which were based on the ratio of monomer to initiator). This indicates that the initiation reactions are somewhat inefficient. With the exception of EB, a precipitant was formed when the monomers were added to the initiator. This could have been due to either (i) the low solubility of the initiator in these monomers, or (ii) some side-reaction(s) leading to partial consumption of the initiator. The mechanism for the polymerization reaction of these epoxide and vinyl monomers is far from certain, although reactions similar to that involving tetrahydrofuran (ECKSTEIN and DREYFUSS, 1979) are feasible.

The molecular weight distributions of the polymers prepared by the $NOPF_6$ initiator are listed in Table I. It is of particular interest to find that under the conditions chosen in this work, the molecular weight of the PnBVE is unusually high while the heterogeneity indices are relatively small. This latter feature is reminiscent of what has been observed (JOHNSON and YOUNG, 1976; MIYAMOTO, et.al., 1984; SEUNG, et.al.) for isobutyl vinyl ether when initiated by iodine or equimolar mixtures of hydrogen iodide and iodine. Conventional ionic initiators at normal temperatures lead to poly(alkyl vinyl ethers) having molecular weights of less than 10^4 (FEE et.al., 1958; PINNER and WORRALL 1959; JOHNSON and YOUNG, 1976). Clearly, in view of the high yield and molecular weight found for PnBVE, the $nBVE/NOPF_6$ system is one which would seem to warrent further study.

In conclusion, we wish to note that the formation of cyclic oligomers in the cationic polymerization of 1,2-epoxides is common (ISHII and SAKAI, 1969). Although the presence of such materials was not indicated in the chromatograms of the polymers, the presence of trace quantities of cyclic oligomers is not excluded for the polyepoxides prepared in this work.

Acknowledgement: This work was supported, in part, by a grant from the Polymers Program, National Science Foundation (grant DMR-79-008299).

TABLE I

Polymerization Reaction Conditions and Molecular Weights

Polymer	Reaction Time (hrs)	Polymer Yield (%)	M_n(exp) 10^{-3}g mol^{-1}	M_n(calc) 10^{-3}g mol^{-1}	$\frac{M_z}{M_w}$	$\frac{M_w}{M_n}$
PSO	48	8	17	9	1.3[a]	1.2[a]
PCHO	48	11	15	11	2.4[a]	2.3[a]
PEB	24	67	16	46	1.5[a]	1.8[a]
PS	48	18	22	18	1.7[b]	2.2[b]
PnBVE	8	95	142	91	1.3[b]	1.6[b]

[a] Via size exclusion chromatography (SEC)

[b] Via the 150C SEC instrument on line with the Chromatix KMX-6 low angle laser light scattering photometer.

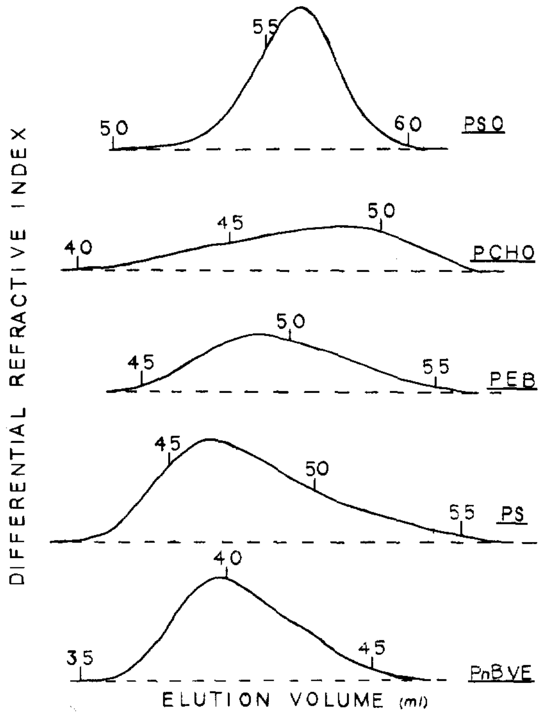

Fig. 1. Chromatographs of PSO, PCHO, PEB, PS and PnBVE.

References

ECKSTEIN, Y. and DREYFUSS, P., J. Polym. Sci. Polym. Chem. Ed., 17, 4115 (1979).

SEUNG, N., FETTERS, L. J. and DREYFUSS, P., paper presented at the 27th IUPAC Internat. Symp. on Macromolecules, Strasbourg, 1981.

MORTON, M. and FETTERS, L. J., Rubber Chem. Tech., 48, 359 (1975).

BRITISH INDUSTRIAL PLASTICS, LTD., Neth. Appl. 6, 509, 888, Feb. 1, 1966; Chem. Abstr., 65, 828d (1966).

BALLIVET-TKATCHENKO, D., BILLARD, C., AND REVILLON, A., J. Polym. Sci. Polym. Chem. Ed., 19, 1697 (1981).

JOHNSON, A. F., and YOUNG, R. N., J. Polym. Sci. Polym. Symp., 56, 211 (1976).

MIYAMOTO, M., SAWAMOTO, M., and HIGASHIMURA, T., Macromolecules, 17, 265 (1984).

SEUNG, S. L. N., YOUNG, R. N., and FETTERS, L. J., unpublished results.

FEE, J.G., PORT, W. S., and WITNAUER, L. P., J. Polym. Sci., 33, 95 (1958).

PINNER, S. H., and WORRALL, R., J. Appl. Polym. Sci., 2, 122 (1959).

ISHII, Y., and SAKAI, S., "1,2 Epoxides" Chapt. 1 in "Ring-Opening Polymerization," K. C. Frisch and S. L. Reegan, Eds, Marcell Dekker, New York, 1969.

Accepted February 11, 1985