NOTES

Graft Copolymers Consisted of Polyether and Phenol-Formaldehyde Resin: A Curable Polyether Resin

Recently, a simple method for preparing graft copolymers of vinyl polymer with a pendant polyether chain has been reported.[1-3] The present paper is concerned with the preparation of a curable graft polyether with a phenol-formaldehyde resin. The method of grafting is almost the same as that described in a previous paper.[1] The epoxy group in the epoxydated phenol-formaldehyde resin was used as a cocatalyst in the polymerization of cyclic ethers such as 3,3-bis(chloromethyl)oxetane (BCMO) and tetrahydrofuran (THF) catalyzed by $BF_3 \cdot O(C_2H_5)_2$.

Phenol-formaldehyde resin (PFR, mol. wt. 520) was prepared through the reaction of phenol and formaldehyde in the presence of hydrochloric acid and then epoxydated with epichlorohydrin to yield an epoxydated PFR.[4] The content of epoxy sites in the epoxydated PFR was determined by the hydrochloric acid–dioxane method.[5]

The polymerizations of BCMO and THF by $BF_3 \cdot O(C_2H_5)_2$ in the presence of epoxydated PFR were carried out in chloroform solution at 0 °C. and in bulk at room temperature, respectively. After being polymerized for a given time, ammoniac methanol was added to the reaction mixture to stop the polymerization. The resulting polymers were then precipitated and washed with methanol or water, followed by drying them in vacuum.

The results of the polymerization of BCMO and THF in the presence of epoxydated PFR and $BF_3 \cdot O(C_2H_5)_2$ are summarized in Tables 1 and 2, respectively.

As can be seen from Tables 1 and 2, it was obvious that epoxydated PFR could act as an excellent cocatlyst for the polymerizations of BCMO and THF by $BF_3 \cdot O(C_2H_5)_2$. All the polymers resulting from BCMO were colorless powders which were soluble in cyclohexanone, indicating that the epoxy site in PFR participated only in the cocatalysis. However, the polymers resulting from THF were colorless waxy materials which partly contained a THF-insoluble polymer.
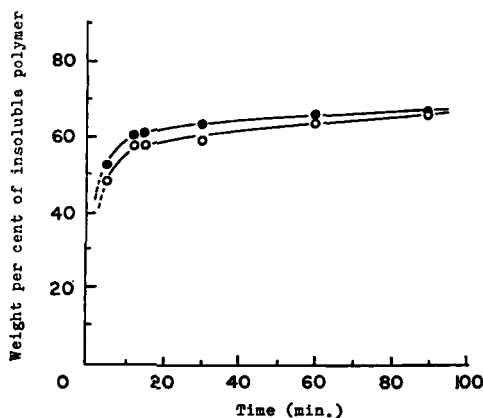

Fig. 1. Curing reaction of unfractionated polymer from BCMO at 170°C. in the presence or absence of HMT. (O) No HMT; (●) 10% HMT.

TABLE I

Graft Polymerization of BCMO onto Epoxydated PFR (0°C.)

Run No.	Epoxyd. PFR, g.	Epoxy content,[a] m. eq./g.	BCMO, g.	$BF_3 \cdot O(C_2H_5)_2$, g.	$CHCl_3$, ml.	Time, min.	Polymer obtained,[b] g.	Epoxyd. PFR in polymer, %	Soluble parts in acetone, %	App. efficiency of grafting,[c] %
1	0.50	1.75	2.5	0.13	5	300	1.83	27.3	15.6	43.1
2	1.00	1.60	5.0	0.23	30	7	1.72	58.1	—	—
3	1.00	4.76	5.0	0.68	30	4	3.66	27.3	12.4	54.6
4	1.00	4.83	5.0	0.69	30	3.7	3.55	28.2	—	—
5	1.00	4.83	5.0	0.69	30	2	3.40	29.4	9.0	69.6
6	6.00	4.76	30.0	2.03	180	37	21.14	28.4	20.3	25.0

[a] Calculated value for a complete epoxydated PFR is 6.27.

[b] All resulting polymers which contained the unreacted PFR were soluble in cyclohexanone at 100°C.

[c] Calculated by the change in weights of epoxydated PFR used initially and extracted by acetone after polymerization.

TABLE II
Graft Polymerization of THF onto Epoxydated PFR (Room Temp.)

Run No.	Epoxyd. PFR, g.	Epoxy content, m. eq./g.	THF, ml.	$BF_3 \cdot O(C_2H_5)_2$, g.	Time, sec.	Polymer obtained,[a] g.	Weight increased,[b] %	Solubility in THF[c]
11	1.00	1.75	20	0.89	40	1.30	30	S.
12	1.00	1.75	20	0.89	105	1.97	97	P.S.
13	1.00	1.75	20	0.25	480	7.55	656	I.
14	1.00	1.75	20	0.25	340	3.40	241	S.
15	1.00	4.83	20	0.69	15	1.10	10	P.S.
16	1.00	4.83	20	0.69	60	1.96	96	P.S.
17	1.00	4.76	20	0.68	10	1.40	40	·P.S.

[a] Contained the epoxydated PFR unreacted.
[b] Based on the epoxydated PFR initially used.
[c] (S.) soluble; (P.S.) partly soluble; (I.) insoluble in THF.

In the case of BCMO grafts, the resulting polymer was extracted with acetone to separate the unreacted or ungrafted PFR; the results are also indicated in Table I. From the decrease in the amount of PFR extracted compared with that of PFR initially used, it might be supported that the graft copolymer was obtained with the apparent efficiencies of grafting as shown in Table I.

Curing the resulting unfractionated polymers, which were a mixture of homopolymer and graft copolymer, was attempted in the presence or absence of hexamethylenetetramine (HMT). The results are shown in Figure 1.

After the curing reaction, the resulting polymers were extracted with acetone and then with cyclohexanone to separate the homopolymers. As seen from Figure 1, the effect of HMT on curing the polymers was not remarkable. However, it was noted that the unfractionated polymers were cured by heating at 170°C. for ten minutes in the absence of HMT. This indicated that unreacted epoxy group in the polymer could also have participated in the cross-linking reaction. The cured polymers thus obtained were completely infusible and insoluble in most organic solvents.

In the case of THF grafts, the separation of pure grafts was unsuccessful, while the unfractionated polymers were easily cured by heating at about 150°C. in the presence or absence of HMT.

References

1. Otsu, T., S. Aoki, and M. Imoto, *J. Polymer Sci.*, B2, 223 (1964).
2. Aoki, S., T. Otsu, and M. Imoto, *Kogyo Kagaku Zasshi*, 67, 971 (1964).
3. Aoki, S., T. Otsu, Y. Harita, and M. Imoto, *Kogyo Kagaku Zasshi*, 67, 1593 (1964).
4. Bradley, T. F., and H. A. Newey, U. S. Pat. 2,716,099 (August 23, 1955); *Chem. Abstr.*, 49, 16526 (1955).
5. King, G., *Nature*, 164, 706 (1949).

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Poly-2-Oxazolidones

Speranza and Peppel[1] recently reported that 2-oxazolidones were formed when mono epoxides and isocyanates are reacted in the presence of tetramethylammonium iodide. They also reported that vinylcyclohexane diepoxide and Epon 828 reacted separately with 2,4-toluenediisocyanate to yield polymeric products which were not further characterized. No other reports have appeared which have described further details on the nature and products of the latter reaction.

This communication outlines an investigation directed toward elucidating the nature of the polymeric products produced when diepoxides react with diisocyanates. In order to obtain information on the conditions and reactions leading to poly-2-oxazolidones, the study of the method of formation of a model compound 3-phenyl-4-phenoxy methyl-2-oxazolidone (I) was first investigated. Heating (0.1 mole) phenylglycidyl ether with