

STUDIES ON THE OXIDATION AND GRAFT COPOLYMERIZATION OF POLYETHERS*

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ABSTRACT

Polyethers could form hydroperoxide under air-oxidation or photo-oxidation in the presence of H_2O_2 . The scission of ether linkage induced by moderate oxidation was prevented by controlling the reaction time and hydroperoxide concentration. The oxidation rate was affected by the end groups of polyethers. The decreasing order of oxidation rate for various poly(tetramethylene ether) glycol derivatives having different end groups are as follows: poly(tetramethylene ether) glycol (PTMG) > poly(tetramethylene ether) acetate (PTMGAC) > poly(tetramethylene ether) phenyl carbamate (PTMGPC). The urethane end groups in PTMGPC increase the resistance toward oxidation. Polyether hydroperoxide reacts with ferrous ion or *N,N*-dimethyl toluidine (DMT) to form polymeric-oxy radical which then initiates the graft copolymerization of vinyl monomers at low temperature, and was devoid of homopolymerization. The copolymer after separation and purification was proved to be a graft one by IR analysis and elemental analysis.

In recent years, some investigations concerning the graft copolymerization of polyether have been reported. The main purpose was focused on the preparation of modified polyurethane. Dunlop^[1] carried out the grafting polymerization of poly(tetramethylene ether) glycol with styrene using *tert*-butyl hydroperoxide at 150°C. Katayama et al.^[2] synthesized graft copolymer of poly(propylene oxide) with acrylonitrile through benzoyl peroxide and *N,N*-dimethyl aniline redox system. Owing to the feasible oxidation property of polyether, we prepared the polyether hydroperoxide at first through controlled oxidation and then the polyether hydroperoxide reacted with ferrous ion or *N,N*-dimethyl toluidine to form redox system which initiates the graft copolymerization of vinyl monomer on polyether. It is obvious that our grafting method in this work possesses two advantages, i.e., the reaction can be performed at rather low temperature and the homopolymerization can be essentially avoided. Since the polyether moieties in poly(ether-urethane) play the role of soft segments, we may take the polyethers with different end groups as the model compounds of soft segments in poly(ether-urethane). Thus our studies on oxidation and graft copolymerization of these polyether derivatives have offered some basic data for oxidation and graft copolymerization of poly(ether-urethane) as well as the corresponding reaction mechanisms. It has been confirmed in our laboratory that this method is also suitable for the preparation of graft copolymer of poly(ether-urethane)^[3].

EXPERIMENTAL

1. Materials

Poly(tetramethylene ether) glycol (PTMG) ($MW=1100$, Japan Soda Co.) was acetylated

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by acetic anhydride to form PTMGACI^[4], or reacted with phenyl isocyanate to form PTMGPC with phenyl carbamate end group. Polyether having acetyl group as one end group and phenyl carbamate group as the other end group i.e., PC (PTMG)AC was also prepared by the above two methods through varying the ratio of the reactants.

2. Thermo-oxidation

6 g. of polyether and a small amount of AIBN were placed into a 150×18 mm filter tube. The tube was then sealed with a stopper fitted with a capillary tube, and put into a water bath at 55°C with air blown by a water pump. A portion of polyether was drawn out at intervals to analyse the content of hydroperoxide using iodometric method.

3. Photo-oxidation

6 g. of polyether was put into a beaker containing 40 ml 30% H₂O₂ solution. The heterogeneous oxidation was carried out with an electromagnetic stirrer at 40–45°C under UV light (500 W Hg lamp). After a certain period the polyether layer was decanted, dissolved in cyclohexane and washed with distilled water until the water layer contained no H₂O₂. Finally, the solvent was evaporated under vacuum at room temperature, and the hydroperoxide content was determined.

4. Graft copolymerization

A certain amount of polyether hydroperoxide was placed in a 150×18 mm test tube, the solution of acrylamide (AAM) or acrylonitrile (AN), methyl methacrylate (MMA) in N,N-dimethyl formamide (DMF) was added and deaerated by nitrogen gas. After the addition of reducing agent ammonium ferrous sulfate, the tube was immersed in a water bath of 40°C for 9 hrs. It was poured into methanol and stirred vigorously to dissolve the ungrafted polyether. Then the solid product was purified by dissolution, reprecipitation and extraction with cyclohexane-benzene mixed solvent for 24 hrs. The graft copolymer was characterized by IR spectra and elemental analysis. When N,N-dimethyl toluidine was used as reducing agent the graft copolymerization of MMA or AN was carried out without adding any solvent. The grafting yield % was calculated as follows:

$$\text{Grafting yield \%} = \frac{\text{The increased weight}}{\text{The weight of polyether}} \times 100$$

RESULTS AND DISCUSSION

1. Oxidation of polyethers with different end groups

Like ordinary ether molecule the macromolecular polyethers are susceptible to oxidation to form hydroperoxide under controlled conditions. The results of oxidation are given in Table 1 and Figs. 1, 2.

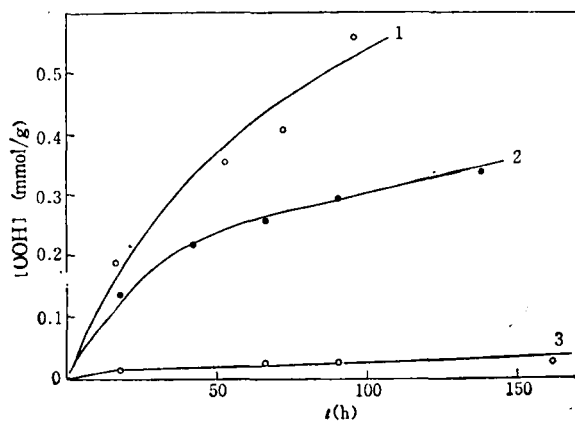
It was shown that either through air-oxidation or photo-oxidation all the polyethers could form hydroperoxides which were characterized and verified by IR spectra (Fig. 3). Photo-oxidation is always faster than air-oxidation, while the latter can be promoted by azobisisobutyronitrile (AIBN). Under same conditions the rates of air-oxidation of different polyethers

Table 1 Oxidation of polyethers¹⁾

No.	Formula		Oxidation time (h)	[OOH] (mmol/g)	[OOH] (mmol/g) after 96 hrs
	Polyether	Catalyst			
0-023	PTMG	0.4% AIBN	96	0.351	0.351
0-024	PTMG	0.8% AIBN	96	0.552	0.552
0-021	PTMG	0	208	0.125	0.080
0-029	PTMGAC	0.4% AIBN	186	0.260	0.189
0-030	PTMGAC	0.8% AIBN	186	0.385	0.320
0-031	PTMGAC	0	210	0.111	0.059
0-045	PC (PTMG) AC	0.4% AIBN	120	0.156	0.159
0-046	PC (PTMG) AC	0.8% AIBN	120	0.210	0.199
0-047	PC (PTMG) AC	0	120	0.0515	0.048
0-032	PTMGPC	0.4% AIBN	313	0.0541	0.0221
0-033	PTMGPC	0.8% AIBN	313	0.0566	0.0290
0-034	PTMGPC	0	402	0.0205	0.0310
0-039 ²⁾	PTMGAC	40 ml 30%	1	0.0562	
0-040 ²⁾	PTMGAC	H ₂ O ₂ used	8	0.145	
0-041 ²⁾	PTMGPC		8	0.0471	

1) Air-oxidation, polyether 6 g., 55°C.

2) Photo-oxidation, polyether 6 g., 40–45°C.

Fig. 1 The air-oxidation of PTMG
55°C, AIBN wt%: 1. 0.8; 2. 0.4; 3. 0

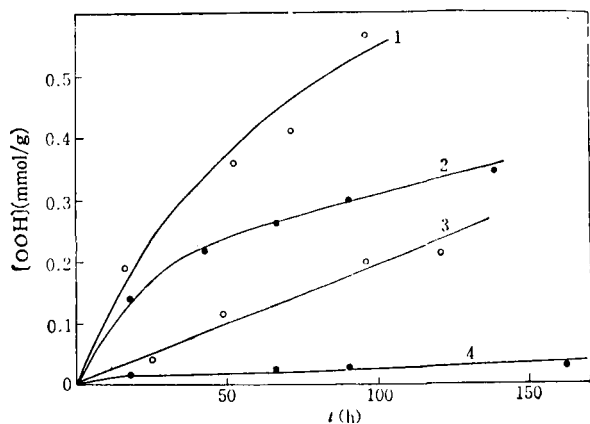


Fig. 2 The air-oxidation of polyethers with different end groups
55°C, AIBN=0.8%.

1. PTMG; 2. PTMGAC; 3. PC(PTMG)AC; 4. PTMGPC.

can be arranged in the following decreasing order: PTMG > PTMGAC > PC(PTMG)AC > PTMGPC. It shows that the urethane end group in the polyether will make its oxidation sluggish. This was ascribed to the formation of hydrogen bond between hydroperoxide and the nitrogen atom in urethane group^[8]. On the other hand, the urethane groups themselves usually form rather strong hydrogen bonds, therefore it will make the polyether more viscous and then cause the oxygen diffusion being difficult.

In order to observe any degradation of polyether during oxidation, both the intrinsic viscosities and IR spectra of polyether before and after oxidation were measured as shown in Table 2 and Fig. 3.

Table 2 The characteristics of polyether hydroperoxide (PTMGHP)

Code	Type	OOH (mmol/g)	$[\eta]$ (dl/g) ¹⁾	IR spectrum at 1720 cm ⁻¹
	PTMG	0	0.0854	No absorption
0-023	PTMGHP	0.35	0.0852	Very weak absorption
0-024	PTMGHP	0.55	0.0835	Weak absorption
0-036	PTMGHP	1.22	0.0492	Strong absorption

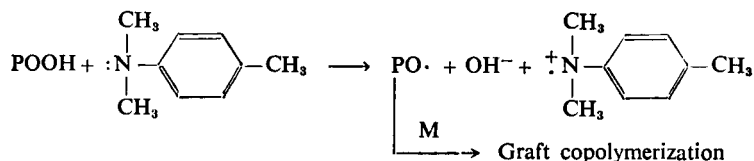
1) Toluene as solvent, 25°C.

Under moderate oxidation condition, the IR spectrum of polyether only revealed a very weak absorption at 1720 cm⁻¹ (carbonyl group). This indicated that the hydroperoxide produced by oxidation would not suffer from further degradation to carbonyl compounds. This was also verified from the negligible change of intrinsic viscosities. Only under severe condition, i.e., the hydroperoxide content increased up to 1.22 mmol/g, the viscosity would decrease sharply and the original polyether changes from the solid wax to sticky liquid at room temperature. Furthermore, the IR spectral absorbance at 1720 cm⁻¹ for carbonyl group became intensive. So we should control the oxidation condition to prevent from degradation.

On the IR spectra of oxidized polyethers, the absorption bands at 3450 cm⁻¹ (OH group)

hydroxyl radical which would lead to homopolymerization. So the redox system was used to prevent the latter reaction. In the presence of ferrous ion, only polymeric alkoxy radical was produced^[8, 9]:

Since we have discovered^[10] that ether hydroperoxide such as tetrahydrofuran hydroperoxide would couple with DMT to form effective redox initiator, thus DMT was also used here:



In the presence of ferrous ion or DMT, the graft reaction of AN or AAM started within one to two minutes at 40°C. It is considered that such graft copolymerization of AN and

Table 3 Graft copolymerization of polyethers

No.	Polyether hydroperoxide ¹⁾			Graft copolymerization ²⁾			
	Polyether	(g)	OOH (mmol)	Reducing agent	(mmol)	Monomer	Grafting (%)
G-020	PTMG	1.00	0.2	DMT	0.4	AAM	152.4
G-021	PTMG	1.00	0.2	DMT	0.4	AN	24.74 ³⁾
G-010	PTMG	1.00	0.3	Fe ²⁺	0.2	AN	125.0
G-016	PTMG	1.50	0.6	Fe ²⁺	0.5	AN	152.8
G-017	PTMG	1.00	0.4	Fe ²⁺	0.3	MMA	54.14 ⁴⁾
G-022	PTMG	1.00	0.2	Fe ²⁺	0.1	AAM	153.1
G-023	PTMGAC	0.69	0.2	Fe ²⁺	0.1	AN	38.78
G-024	PTMGAC	0.69	0.2	Fe ²⁺	0.1	MMA	7.99
G-025	PTMGAC	0.69	0.2	Fe ²⁺	0.1	AAM	215.9
G-027	PTMGAC	0.69	0.2	DMT	0.4	AN	10.84 ³⁾
G-028	PTMGAC	0.69	0.2	DMT	0.4	MMA	2.77
G-029	PTMGAC	0.69	0.2	DMT	0.4	AAM	91.46
G-030	PTMGPC	1.70	0.1	Fe ²⁺	0.1	AN	51.18
G-032	PTMGPC	1.70	0.1	Fe ²⁺	0.1	AAM	65.51
G-033	PTMGPC	1.70	0.1	DMT	0.4	AN	76.61 ³⁾
G-035	PTMGPC	1.70	0.1	DMT	0.4	AAM	66.57
G-063	PTMGAC	0.62	0.09	Fe ²⁺	0.1	AN	20.63
G-064	PTMGAC	0.62	0.09	Fe ²⁺	0.1	AAM	107.1
G-046	PTMGPC	1.70	0.08	Fe ²⁺	0.1	AN	32.58
G-047	PTMGPC	1.70	0.08	Fe ²⁺	0.1	AAM	18.91

1) Polyether hydroperoxide used in G-046, G-047, G-063 and G-064 were prepared by photo-oxidation, the rest were prepared by air-oxidation.

2) 4 ml of AN or MMA, 2 g. of AAM were used respectively, 40°C, 9 hrs.

3) The graft reactions were carried out in dark.

4) Methanol was used as solvent.

AAM are very effective except MMA which showed some reluctance towards grafting. The data of graft copolymerization are summarized in Table 3.

Similarly, poly(ethylene oxide) hydroperoxide could be also prepared by air-oxidation. It coupled with ferrous ion to initiate AN graft copolymerization producing P(EO-g-AN) copolymer with 66% grafting yield.

As the other conditions are fixed the grafting yield would increase with increasing of OOH concentration. The grafting yield would vary with the change of DMT concentration. In general the grafting yield would increase as the reaction time increases under certain condition. The data are summarized in Table 4.

Table 4 AAM graft copolymerization on PTMG

No.	Polyether (g)	OOH (mmol)	DMT (mmol)	Fe ²⁺ (mmol)	Induction period (min)	Reaction time (h)	Grafting (%)
G-051	1.0	0.03		0.10	0	9.0	33.75
G-052	1.0	0.09		0.10	0	9.0	36.11
G-022	1.0	0.20		0.10	0	9.0	153.1
G-067	1.0	0.085	0.035		10	9.0	35.71
G-066	1.0	0.085	0.070		7	9.0	49.85
G-068	1.0	0.085	0.14		4	9.0	29.81
G-069	1.0	0.085	0.40		3	9.0	44.46
G-059	1.0	0.10		0.10	0	1.0	71.31
G-056	1.0	0.10		0.10	0	2.0	89.40
G-055	1.0	0.10		0.10	0	5.0	127.7
G-045	1.0	0.10	0.40		2	1.0	A little
G-044	1.0	0.10	0.40		2	2.0	1.52
G-043	1.0	0.10	0.40		2	5.0	27.24

AAM 2 g., DMF 10 ml, 40°C.

3. Characterization of graft copolymers

The unreacted polyether, mainly the polyether without OOH group could be removed by its dissolution in methanol. The calculated amount of unreacted polyether could be entirely recovered by a series of separations and the graft copolymer was obtained. In the absence of polyether hydroperoxide the vinyl monomer such as AN could not polymerize by the action of ferrous ion or DMT alone. Thus, it was graft copolymerization that took place in the presence of both polyether hydroperoxide and the reducing agent without any homopolymerization. This was confirmed likewise through precipitation fractionation of the copolymer obtained.

The formation of graft copolymer was verified further by IR spectra. For example, on the IR spectrum of poly(TMGAC-g-AN) the absorption bands of C—O—C ether linkage at 1105 cm⁻¹, carbonyl group of polyether end at 1720 cm⁻¹ and C≡N group at 2250 cm⁻¹ all occurred at the same time (Fig. 4). Similarly, the absorption bands of C≡N group and C—O—C group were also found from the IR spectrum of P(EO-g-AN) copolymer. In the case of P(TMGAC-g-AAM), the absorption of carbonyl group at polyether end could not be distinguished due to the interference of amide absorption at 1660 cm⁻¹. However, the absorption band of C—O—C group at 1105 cm⁻¹ still appeared.

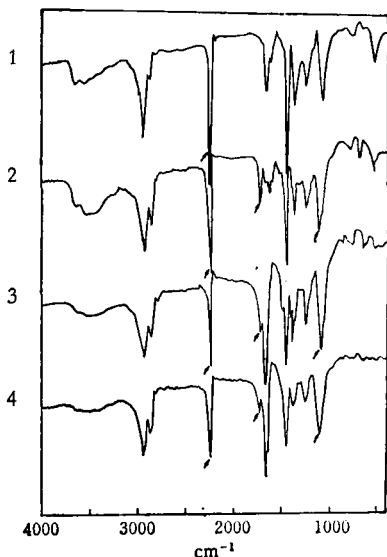


Fig. 4 The IR spectra of PAN and P(TMGAC-g-AN)
1. PAN homopolymer;
2. P(TMGAC-g-AN), before fractionation;
3. P(TMGAC-g-AN), after fractionation, No. 1;
4. P(TMGAC-g-AN), after fractionation, No. 2.

The results of elemental analysis showed that the nitrogen content of graft copolymer was lower than PAN homopolymer, such as the nitrogen content of P(TMGAC-g-AN) was 23.3%, while that of PAN is 26.4%. The decrease of nitrogen content was caused by the participation of polyether.

We have carried out the precipitation fractionation of P(TMGAC-g-AN) and two frac-

Table 5 The nitrogen content of polymers

Polymer	N (%)
PAN	26.40 (Calculated)
P(TMGAC-g-AN)	23.31 (Found before fractionation)
P(TMGAC-g-AN)	23.30 (Found after fractionation, No. 1)
P(TMGAC-g-AN)	22.85 (Found after fractionation, No. 2)

tions were obtained. From IR spectra and elemental analysis data it was revealed that both the fractions were not the homopolymer of AN. So the graft copolymerization without any homopolymerization was also verified.

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