

STUDIES ON THE OXIDATION AND GRAFT COPOLYMERIZATION OF POLY(ETHER-URETHANE)*

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ABSTRACT

A new method of graft copolymerization of acrylamide (AAM) on poly(ether-urethane) (PEU) which was prepared from poly(tetramethylene ether) glycol (PTMG), 4,4'-diphenylmethane diisocyanate (MDI) and ethylene diamine or butanediol extender was investigated. Hydroperoxide group was first introduced onto the surface of PEU through photo-oxidation in the presence of hydrogen peroxide, then it was reacted with ferrous ion or N,N-dimethyl toluidine (DMT) to initiate AAM graft copolymerization on PEU surface. The graft reaction could be carried out effectively at low temperature. The formation of graft copolymer has been verified by its water absorption % and the scanning electron microscopy photographs. Some model compounds of PEU soft segment and hard segment were synthesized in order to clarify the site of graft reaction. The results of oxidation and graft copolymerization of model compounds showed that this graft copolymerization possesses higher selectivity, and it takes place predominately at the polyether segments, because the ether linkage in soft segment is very sensitive to oxidation and can form hydroperoxide easily. Thus, the grafting site appears to be at α -carbon of the ether linkage.

Poly(ether-urethane) (PEU) with linear segmented chain structure is known as a kind of thermoplastic elastomers (TPE). Polyether segment in PEU acts as the "soft segment", while the segment formed from diisocyanate and chain extender is usually called the "hard segment". Since PEU possesses fair anti-coagulating (non-thrombogenic) properties and good mechanical behavior, it has been the candidate material for artificial heart or kidney and blood vessels. Recently, some hydrophilic monomers such as acrylamide (AAM) and 2-hydroxyethyl methacrylate were grafted onto PEU surface in order to enhance the non-thrombogenic properties of PEU^[1]. The main methods of graft copolymerization on PEU include: radiation induced grafting^[2], active vapor method^[3] and ceric salt initiation method^[4-5]. However, either the graft mechanism or its grafting site still remains unclear and has not been reported yet. In order to search the relation between the structure and properties of PEU graft copolymer, we have devised a new method of graft copolymerization^[6], i.e., selective grafting through controlled oxidation on PEU film. In order to clarify the mechanism, studies on the oxidation and graft copolymerization of PEU with model compounds were carried out. Our results show that the graft reaction takes place predominately at the polyether segments.

EXPERIMENTAL

1. Materials

4,4'-diphenylmethane diisocyanate (MDI) (Bayer Co.) was purified by distillation

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under reduced pressure. Poly(tetramethylene ether) glycol (PTMG) with molecular weight 1100 (Japan Soda Co.) was dried in vacuum at 100°C. *N,N*-dimethyl toluidine (DMT) was synthesized in this laboratory. *N,N*-dimethyl formamide (DMF) and other solvents were all chemical reagents and purified by usual methods. Acrylamide (AAM) was recrystallized in acetone for three times, m.p. 84°C.

2. Synthesis and film casting of PEU

A variety of PEU was prepared according to [7]. Their composition and code are listed in Table 1. In a code like PEU-4-1100-B, the number 4 denotes the number of carbon atoms per PTMG unit, the second number 1100 denotes the molecular weight of PTMG and the final letter B expresses the chain extender (B, butanediol, E, ethylene diamine). The formula of PEU is as follows:

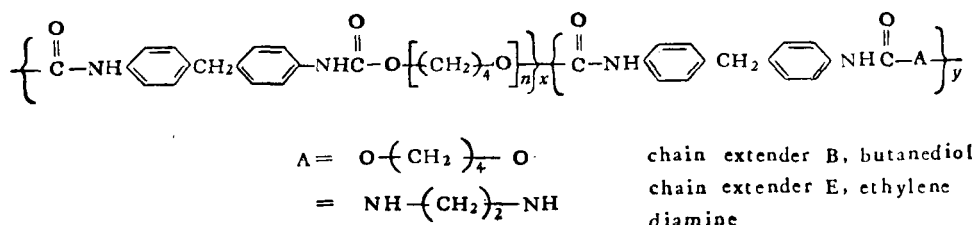


Table 1 PEU code and formulas

No.	PEU code	Formula				Intrinsic viscosity [η] (dl/g)
		MDI	PTMG	Ethylene diamine	Butanediol	
906	PEU-4-1100-B	2	1		1	0.557
907	PEU-4-1100-B	2	1		1	0.480
104	PEU-4-1900-B	3	1		2	0.792
8106	PEU-4-1100-B	2	1		1	0.435
8003	PEU-4-1100-B	2	1		1	0.700
8107	PEU-4-1100-B	2	1		1	0.840
7979	PEU-4-1100-E	2	1	1		0.854
S-001	PEU-4-1100-E	2	1	1		0.548
S-003	PEU-4-1100	2	1			0.667

PEU was dissolved in DMF and then poured into a glass mould. The solvent was slowly evaporated at 50°C, the PEU film was dried in vacuum at 50°C to a thickness around 0.2 mm.

3. Oxidation and graft copolymerization of PEU film

A piece of PEU film ($\sim 2 \times 4 \text{ cm}^2$) which had been dried and weighed was immersed in a DMF-H₂O mixed solvent for 12 hrs at 40°C. It was taken out and washed with water and then placed into a beaker containing 40 ml H₂O₂(30%) solution. The oxidation reaction was carried out for 24 hrs at room temperature under UV irradiation (500 W Hg lamp). After washed with distilled water several times, the oxidized PEU film was put into a 10%

AAM aqueous solution (or DMF-H₂O mixed solution), which was then deaerated with nitrogen gas. DMT or ferrous salt was added and the reaction maintained at room temperature for about 20–30 min with stirring. To calculate the grafting yield the grafted PEU film was dried and weighed after extraction with boiling water for 72 hrs. The water absorption was determined according to the procedure described in the previous paper^[5]. The surface morphology of the grafted PEU film was observed by scanning electron microscopy (SEM).

4. Synthesis and oxidation of PEU model compounds

Model compounds of PEU soft segment with different end groups such PTMGAC with acetate groups and PTMGPIC with phenyl amino-formyloxy end groups were synthesized from PTMG^[8]. Polyether having one acetyl group and one phenyl amino-formyloxy end group respectively was also prepared. Model compound U-I was made from MDI and PTMG derivative with one free hydroxyl end group and other acetate end group. The model compounds of hard segment were prepared from MDI and ethylene diamine, butanediol or methanol respectively (their structures are shown in the next section). The oxidation of the model compounds was carried out as described above.

RESULTS AND DISCUSSION

1. Oxidation and graft copolymerization of PEU

Through photo-oxidation the PEU film, such as 907 and 8106 in Tables 1 and 2, have hydroperoxide groups formed on the surface in the amount of 0.04–0.09 mmol / g PEU. After oxidation the PEU films remain soluble as before without any obvious change in color and intrinsic viscosity. The hard segment model compound PU-III is more stable toward photo-oxidation, while sample S-003 shows much decrease in viscosity. The above facts indicate that photo-oxidation of PEU films usually occur on the ether linkage and can be controlled to a degree without any obvious degradation. Thermo-oxidation of PEU films by air always proceed more slowly to introduce —OOH group.

Table 2 Intrinsic viscosity of PEUs (in DMF, 30°C)

Substrate	907	8106	S-003	PU-III
[η] (dl / g) before oxidation	0.480	0.435	0.677	0.503
[η] (dl / g) after oxidation	0.431	0.447	0.511	0.501

The oxidized PEU film extended by diol or diamine will react with ferrous ion or DMT as redox system to initiate AAM graft copolymerization. The results of AAM graft copolymerization are summarized in the Table 3.

Table 3 AAM graft copolymerization onto PEU film¹⁾

PEU ²⁾ type	Reducing agent	Film weight (g)	Graft (%)	Graft (PAAM mg / cm ²)	Water uptake (%)	Water in graft layer (mg/cm ²)	SEM graph
PEU-4-1100-B (8003)	DMT ³⁾	0.0440			7.0		
PEU-4-1900-B (104)	DMT ⁴⁾	0.0669	3.89	0.59	22.9	86.0	
PEU-4-1100-E (7979)	DMT ⁵⁾	0.0178	0.56		22.4	97.6	
PEU-4-1100-B (8107)	DMT ⁴⁾	0.0872	0.69		20.8	96.6	
PEU-4-1100-B (8003)	Fe ²⁺	0.0940	0.21		11.0	97.8	
PEU-4-1100-B (906)	Fe ²⁺	0.0710	1.69		8.20	83.1	
PEU-4-1100-B (8107)	Fe ²⁺	0.0735	8.3		86.6	91.9	
PEU-4-1100-E	Fe ²⁺	0.0320	2.50		55.0	95.5	a
PEU-4-1100-E (7979)	Fe ²⁺	0.0517			30.5		b
PEU-4-1100-E (S-001)	Fe ²⁺	0.0481	1.46		14.5	82.5	
PEU-4-1100 (S-003)	Fe ²⁺	0.0924	1.21	0.22	21.5	94.8	
PEU-4-1100 (S-003)	Fe ²⁺	0.0625	1.12	0.14	37.2	97.1	
PEU-4-1100-E (S-001)	Fe ²⁺ 6)	0.1251	5.12	1.16	78.5	94.2	
PEU-4-1100-B (907)	Fe ²⁺ 6)	0.1754	9.64	2.11	35.5	80.1	
PEU-4-1100-E (7979)	Fe ²⁺	0.0242	1.24		17.2	93.3	

1) 10% AAM aqueous solution 15 ml, ferrous ammonium sulfate 40 mg, polymerization at room temperature, 20–30 min; or AAM 1.5 g, DMT 48 mg., polymerization at 40°C, 20 min.

2) PEU film were oxidized with H₂O₂ under UV light at room temperature, 24–34 hrs.

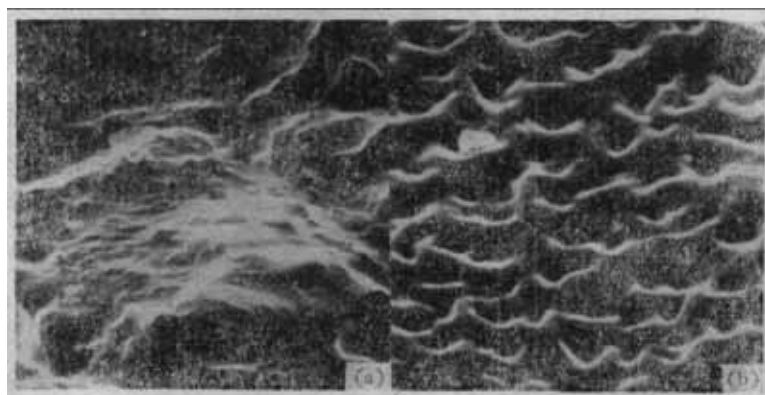
3) DMF / H₂O (2 / 1 by vol.) 15 ml was used as mixed solvent.

4) DMT 32 mg, 10 ml water used as solvent.

5) DMF / H₂O (1 / 2 by vol.) 15 ml was used as mixed solvent.

6) 10% AAM aqueous solution 25 ml, other conditions as note 1).

The original PEU films are always transparent, smooth and low water-absorbing (2–3%), while the grafted PEU films become opaque, rough and much higher water-absorbing (7–35%). From the SEM graphs of the grafted PEU films (see Fig. 1) various salient features due to graft copolymerization of AAM on the surface are observed. Furthermore, we have analysed the composition of PEU surface by ESCA technique and found that its nitrogen content was increased after grafting. It was caused by the higher nitrogen content of PAAM layer compared with the PEU substrate. All of the above results verified the formation of



a (× 530)

b (× 480)

Fig. 1 SEM graphs of grafted PEU films

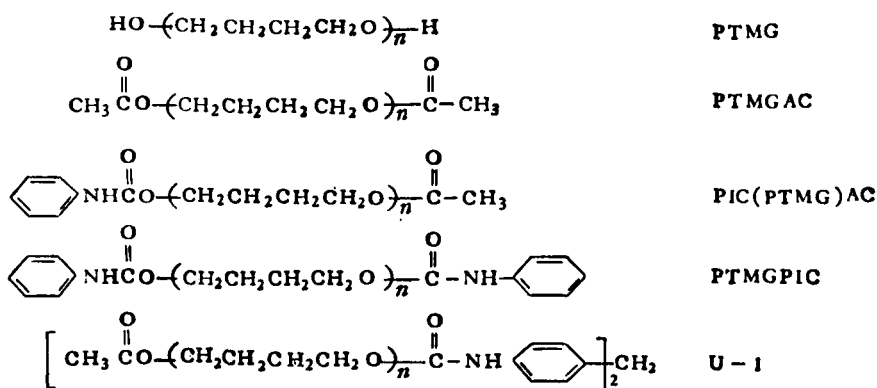
graft copolymer on the PEU film.

Though the grafting yield of PEU prepared by this new method is not the highest as compared to those reported in the literature, e.g., radiation initiation would give grafting yield more than 100%^[2], it matches with the grafting yield in the ceric salt initiation method^[6]. For example, the grafting yield of PEU film prepared by this method is 2–9% and water absorption is 7–35%, while the grafting yield by ceric salt initiation is 3–9% and water absorption 10–38%. In this new graft method the contact angle of grafted PEU with water was lowered from 68–78° to 45–57°, while the ceric salt initiation method gave a similar range of 41–45°. This shows that the hydrophilicity of the PEU film is always increased through AAM grafting; therefore, it is expected that the non-thrombogenic properties of the films can be improved. These two different initiation methods have same reaction characteristics in common, both perform the copolymerization at rather low temperature. But the reaction period of the new method is much longer than that of the ceric salt initiation method, as a result of longer oxidation period in the first step. However, the grafting site of new method has been clarified as shown below. This will facilitate the further investigation on the relation between the structures and properties of the graft copolymers.

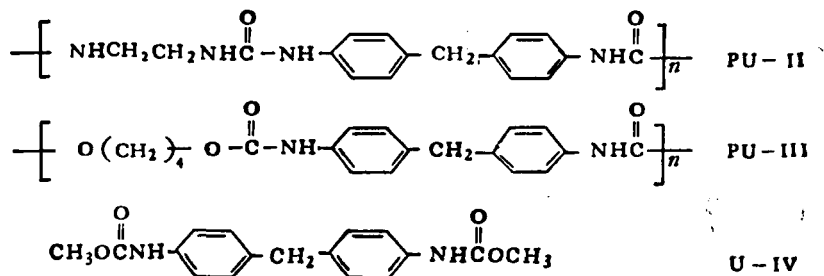
2. Mechanism and reaction site of graft copolymerization

In order to clarify the graft reaction mechanism we synthesized some model compounds of PEU as follows:

Model compounds of PEU soft segment:



Model compounds of PEU hard segment:



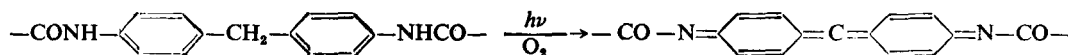
We have presented the main results of oxidation and graft copolymerization of model compounds of PEU soft segment in the previous paper^[8]. It was found that the model compounds of soft segment containing polyether chain formed hydroperoxide easily either under air-oxidation or photo-oxidation, which then initiated graft copolymerization of vinyl monomers through its redox reaction with ferrous ion or DMT. The rate of oxidation of polyether decreased obviously when the urethane linkage was introduced into polyether chain. It is clear that the urethane group in the hard segment could enhance the stability of the macromolecule towards oxidation^[9]. Therefore, the oxidation behavior of model compounds of hard segment was investigated and the results are given in Table 4.

Table 4 Photo-oxidation of model compounds (30% H₂O₂)

No.	Type	Oxidation reaction			
		T (°C)	Time (h)	OOH (mmol / g)	
0-039	PTMGAC	40-45	1.0	0.0562	PTMGAC $[\eta] = 0.0832$ (before oxidation) $[\eta] = 0.0828$ (after oxidation)
0-040	PTMGAC	40-45	8.0	0.145	
0-041	PTMGPIC	40-45	8.0	0.0471	
0-051	U-I	40-45	8.0	0.0314	
0-048	U-IV	40-45	8.0	0.0894	
0-049	PU-II	40-45	8.0	0	
0-050	PU-III	40-45	8.0	0.0105	
0-054	U-IV	20-25	24.0	0	
0-052	PU-II	20-25	24.0	0	
0-053	PU-III	20-25	24.0	0.0116	

In the case of hard segment models, the oxidation became difficult since the polyether segment was absent. The hydroperoxide contents of PU-III and U-IV were less than 1/4-1/3 of that PTMGPIC and U-I. Furthermore, PU-II having uric structure could hardly form any hydroperoxide. This conforms with the fact that uric linkage is more resistant to oxidation than urethane linkage^[10]. Even though the oxidation time was prolonged to 24 hrs the hydroperoxide content was still kept at low level. Obviously, the hard segment possesses good resistance to oxidation. So it is reasonable to propose that the oxidation reaction took place predominately at polyether soft segment, i.e., at the α -carbon of the ether linkage. Recently, Hoeschele^[11] reported that in the oxidation of polyether-polyester block copolymer the reaction position was also at the α -carbon of the ether linkage.

In addition, Allen et al.^[12] reported that the $-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-$ group in PEU could be converted to chromogen through long-time photo-oxidation (>100 hrs) as follows:



However, the colors of the PEU film, PU-III and U-IV were not changed under low temperature and short duration conditions. This revealed that $-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-$

group did not participate in the oxidation.

The results of oxidation and graft copolymerization of the model compounds show that our graft copolymerization on PEU films possesses higher selectivity, and it takes place predominately at the polyether segment with the grafting site at the α -carbon of the ether linkage.

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