

SYNTHESIS OF POLYESTER-POLYETHER MULTIBLOCK COPOLYMERS FROM POLYESTERS

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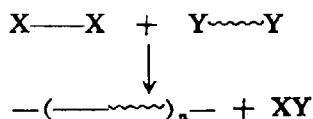
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ABSTRACT

A polymeric method was explored for the preparation of polyester-polyether multiblock copolymers using polyesters and polyethers as starting materials. The mechanism of the reaction and the effect of the segment structure on it, the segment sequence of the block copolymers prepared have been studied. It has been shown that to the polymeric method the degree of compatibility between starting polyester and polyether is of paramount importance, which determines not only the compositional homogeneity of the block copolymers formed but also the success of the polymeric method to get the block copolymers of the expected structure.

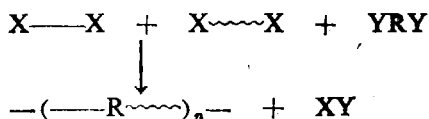
$-(A-B)_n$ -type multiblock copolymers are usually synthesized from difunctional monomers or oligomers by condensation reaction. The methods generally used can be summarized as follows:

1. Interaction of oligomers bearing mutually reactive end groups:



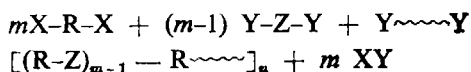
The multiblock copolymers obtained by this method are characterized by alternating sequence distribution.

2. Coupling of two oligomers with the same functional end groups:



By this method the integrity of block copolymers obtained depends on the similarity of oligomers in reactivity toward the coupling agent. If oligomers used are dissimilar in their reactivity the long run of similar segments can be formed due to the ability of one oligomer to couple with itself.

3. Polycondensation of monomers in the presence of oligomer:



The monomer X-R-X here may react with both monomer Y-Z-Y and the oligomer with the same functional end group Y ~~~~ Y to get the multiblock copolymers. The compositional homogeneity of such block copolymer is dependent upon the degree of compatibility of segments^[1].

All methods mentioned above are using oligomers or monomers as starting materials and the reactions have also been intensively studied.

This paper describes a "polymeric method" using polymers as starting materials for synthesizing multiblock copolymers of moderately defined structure. To this method, little study has been published beside patent literature about the preparation of polyethylene terephthalate-polyethylene glycol multiblock copolymer (PET-PEG) from polyethylene terephthalate (PET) and polyethylene glycol (PEG)^[2]. As polyester-polyether multiblock copolymers are a class of very useful thermoplastic elastomer and a variety of polyester-polyether multiblock copolymers can be obtained by combinations of different polyester hard segment and polyether soft segment^[3, 4], in the present work the synthesis of polyester-polyether multiblock copolymers with different segment structures using the polymeric method are explored to see what combinations of segments are the most suitable to this method. The mechanism of the block copolymerization reaction as well as the segment sequence distribution of the block copolymers obtained will be also dealt with.

EXPERIMENTAL

Model compound poly(polytetramethylene glycol terephthalate) was synthesized by polycondensation of polytetramethylene glycol (PTMG) of *MW* 2000 and N,N'-terephthaloyl-bis- ϵ -caprolactam at 200°C. Experimental details have been reported elsewhere^[5].

¹H-NMR spectra were obtained on 250 MHz NMR spectrometer at 3000 Hz sweep width, using CDCl₃ as solvent and TMS as internal standard. ¹³C-NMR spectra were obtained on JEOL FX 100 NMR spectrometer, sweep width 3000 Hz, 90° pulse, proton-noise-decoupled, CDCl₃ was taken as solvent and internal standard (76.94 ppm). Samples were extracted by C₂H₅OH before determination.

Mechanical properties were examined on an Instron model 1122 instrument at room temperature. The samples were cast from 5% CHCl₃ solution dried in vacuum at 40°C and then annealed at 120°C.

RESULTS AND DISCUSSION

Reaction of block copolymerization

The method of synthesizing polyester-polyether multiblock copolymers directly from PET or PBT (polybutylene terephthalate) and a polyether as starting materials will be referred in the following as the "polymeric method". The conventional method using dimethyl terephthalate (DMT) and ethylene glycol (or butylene glycol) and a polyether to get the polyester-polyether multiblock copolymers (as the method 3 mentioned in the introduction) will be referred as the "monomeric method".

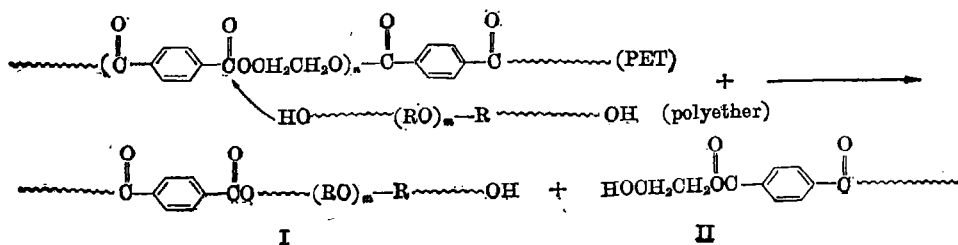
The preparation of multiblock copolymers by the polymeric method was carried out as follows: Commercial PET or PBT ($[\eta]$ 0.6–0.9 dl/g) was first molten with hydroxy-termi-

nated polyether (MW 1000–2000) in the presence of catalysts (such as TiO (COO $COOK$)₂ and Zn (OAc)₂) at $260^{\circ}C$ for 1 hr with stirring and with N_2 bubbling continuously through the mixture, then polycondensation reaction was conducted under vacuum 0.01 torr at $265^{\circ}C$ for 2 hrs. With proper combination of segment structures polyester-polyether multiblock copolymers of $[\eta]$ higher than 1.4 dl/g (in *m*-cresol at $30^{\circ}C$) could be obtained.

For the above reaction process, a mechanism involving alcoholysis and polycondensation reaction has been proposed as follows:

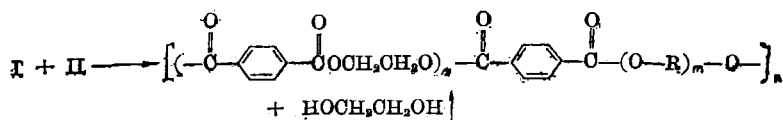
(1) Alcoholysis

In the melt of polyester and polyether in the presence of catalysts, the hydroxy end groups of polyether will attack the ester linkage in macromolecular chains of the polyester. As a result, the polyester chain will be chopped thus reducing the molecular weight of the polyester dramatically.



(2) Polycondensation

The polyester-polyether multiblock copolymers were obtained by polycondensation of I and II produced in the first step and small molecular glycol was splitting off at this stage.



The overall reaction process mentioned above can be described as the exchange of the small molecular glycol moiety of a polyester with a polyether glycol. This process was confirmed by IR. If PET was used as starting material, the distillate of reaction was identified

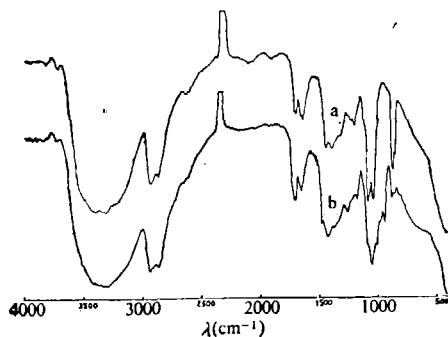


Fig. 1 IR of distillate of the polycondensation
(a) PET and PTMG as starting materials;
(b) PBT and PTMG as starting materials.

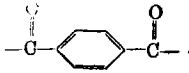
by IR to be ethylene glycol (absorption at 1080 cm^{-1} and 3400 cm^{-1}), while butylene glycol was found (absorption at 1050 cm^{-1} and 3400 cm^{-1}) in the case of using PBT (see Fig. 1).

The polyester-polyether multiblock copolymers obtained were extracted by ethanol and then dissolved in CDCl_3 for $^1\text{H-NMR}$ examination to ascertain the block structures, as the block copolymers are soluble in CHCl_3 , while the starting polyesters are insoluble in it, and the starting polyethers are soluble in ethanol. It has been shown by $^1\text{H-NMR}$ that the aromatic protons of polyester have a sharp singlet at δ 8.05 ppm. The chemical shift of CH_2 protons in polyesters changes with structure of polyesters, PBT at 4.3–4.4 ppm, PET at 4.64 ppm. The peak at 4.3 ppm was assigned to the linkage of PET segment with PTMG segment. The chemical shift of CH_2 , located at α position of ether oxygen, changes with polyether structure, δ 3.4 ppm in PTMG and δ 3.6 ppm in PEG segment.

Segment sequence distribution

In the case of monomeric method, DMT can react with both glycol and polyether glycol, and as a result the long run of soft segment can be formed^[6]. In the case of polymeric method, the segment sequence should depend on the position along the chain of polyester, to which the hydroxy end groups of polyether has attacked. It is interesting to see if such a long soft segment sequence could also occur by polymeric method. $^{13}\text{C-NMR}$ has been used to analyze the sequence distribution of the block copolymers synthesized by the polymeric method, based on the chemical shift of aromatic quaternary carbons. A sample containing 21wt% of PET segment, 79 wt % of PTMG of MW 1000, was examined and the results obtained showed the presence of quadruplet peaks of the aromatic quaternary carbons (Fig. 2). These four peaks were assigned to four possible triad sequences in multiblock copolymers obtained, as follows:

Peaks	Triad	δ (ppm)
b	E-T-E	133.396
a	P-T-E (P side)	133.061
d	E-T-P (E side)	134.127
c	P-T-P	133.784

Where T, P, E, represent , and $-(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_n-\text{O}-$ — $\text{OCH}_2\text{CH}_2\text{O}-$ respectively.

Obviously, E-T-E triad corresponds to PET structure, E-T-P (or P-T-E) triad to the linkage of PET with PTMG and the P-T-P triad to the long run sequence of polyether segment formed from two PTMG connected by a terephthaloyl residue. The chemical shift of P-T-P triad was confirmed by that of poly(polytetramethylene glycol terephthalate) as the model compound (Fig. 3). Its $^{13}\text{C-NMR}$ spectrum showed a singlet peak at δ 133.784 ppm, coincident with the peak c in Fig. 2. The existence of P-T-P triad demonstrated that the long run sequence of soft segment could also formed in the polyester-polyether multiblock copolymers made by the polymeric method and therefore the multiblock copolymers obtained by the polymeric method have similar random block structure as that prepared by monomeric

method^[6].

Effect of segment structures

It has been reported in our previous work that in the case of monomeric method, the predominate effect of the segment structure on the block copolymerization and the compositional homogeneity of block copolymers obtained was the effect of the degree of segment compatibility. The order of segment compatibility has been given as follows^[1]:

For the same soft segment PBT > PET

For the same hard segment PEG > PTMG > (PPG-PTMG) > PPG

For elucidation of the effect of segment structure on the polymeric method, a series of polyester-polyether block copolymers were synthesized shown in Table 1. Their compositional homogeneity was evaluated roughly by the solubility test. Large amounts chloroform insoluble fraction and ethanol soluble fraction can be separated from the samples of less compositional homogeneity. The CHCl_3 insoluble fraction has been shown by IR spectra to be an unreacted homopolyester or it may be a copolymer having much higher content of the hard segment than the average. The ethanol soluble fraction was shown to be low molecular weight copolymers with high polyether content by comparing the intensities of C—O—C vibration at 1120 cm^{-1} with $=\text{C—O—}$ vibration at 1270 cm^{-1} ^[11].

Since PBT is more compatible with polyethers than PET, it is expected that the use of PBT to react with PTMG or PEG in the polymeric method will give PBT-PTMG and PBT-PEG multiblock copolymers of good compositional homogeneity and have no CHCl_3 insoluble fraction. In the case of PET, due to its lower compatibility with polyethers, the polymeric method has limited applications. The use of PET to react with PTMG of MW 2000 can not get PET-PTMG with expected compositional homogeneity, and the $[\eta]$ is low. However when the MW of PTMG is low, for example MW 1000, PET-PTMG block copolymer with anticipated composition and $[\eta]$ 1.4 dl/g could be obtained. This could be understood as the compatibility increases with decreasing molecular weight of segments. At the same, an increase in the concentration of hydroxy end groups of the lower molecular weight polyethers will accelerate the alcoholysis reaction of polyester during first reaction step. Attempts to prepare block copolymers from polypropylene glycol copolyether (PPG-PTMG) with PBT or PET were unsuccessful because of poor compatibility, although these block copolymers could be synthesized by "monomeric method". PBT or PET could not react with polypropylene glycol (PPG) at all, because they are completely immiscible at the reaction temperature.

The results obtained demonstrate that the degree of compatibility between starting polyester and polyether is of paramount importance to the polymeric method to assure compositional homogeneity of the block copolymers formed and the success of the method to get the block copolymers of expected structure.

Segment ratio control

The segment ratio directly influences the properties and also the morphology of multiblock copolymers obtained. A comparison of the segment ratio as calculated from the ratio of starting materials and that determined by $^1\text{H-NMR}$ is listed in Table 2. It is evident that the more compatible system PBT-PTMG, PBT-PEG and PET-PTMG (1000) with lower

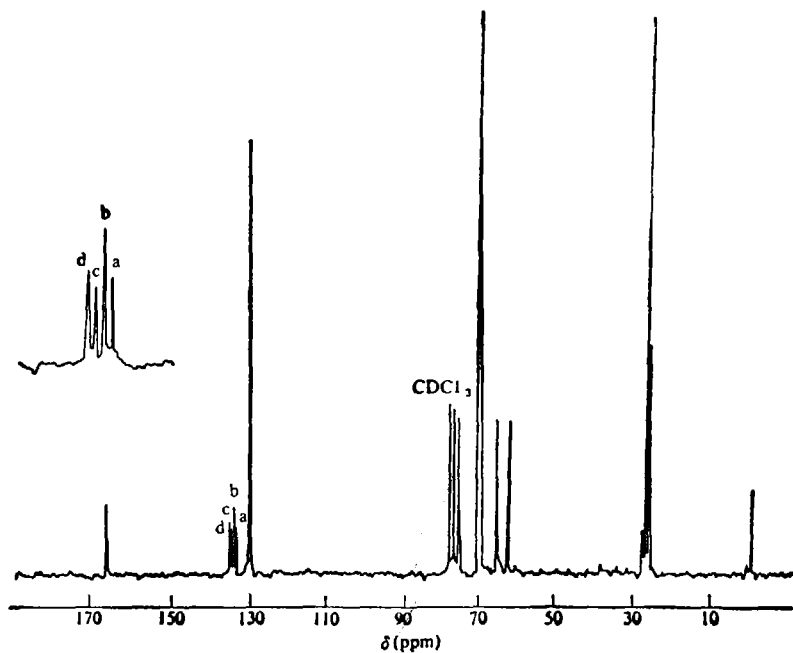


Fig. 2 ^{13}C -NMR of PET (21)-PTMG (1000) block copolymer

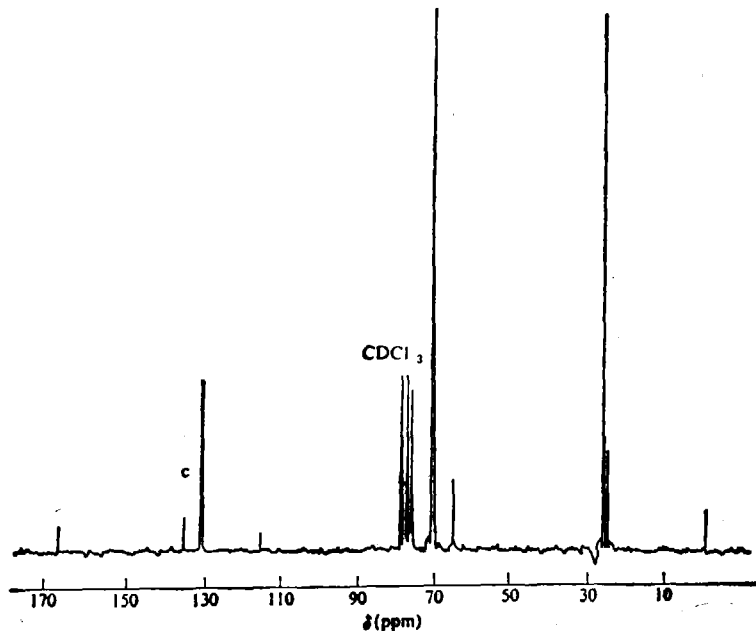


Fig. 3 ^{13}C -NMR of poly(polytetramethylene glycol terephthalate) having structure:

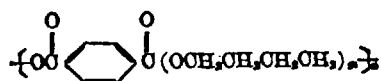


Table 1 Different segment combinations

No. Segment structures	Polyester* (wt %)	MW of polyether	$[\eta]$ (dl/g)	CHCl ₃ insoluble (%)	C ₂ H ₅ OH soluble (%)	m.p.(°C)
1. PBT-PTMG	21	2000	1.3	0	5.70	159—162
2. PBT-PTMG	30	2000	1.86	0	1.47	172—178
3. PBT-PTMG	40	2000	1.73	0	1.37	207—211
4. PBT-PEG	30	2000	1.40	0	4.20	155—160
5. PET-PTMG	21	2000	0.77	0	45.6	—
6. PET-PTMG	30	2000	0.92	10.4	12.3	—
7. PET-PEG	30	2000	1.02	6	25.6	213—227
8. PET-PTMG	21	1000	1.41	0	9.5	148—156
9. PET-PTMG	30	1000	1.46	0	5.8	178—184
10. PBT-(PPG-PTMG)	21	2000	0.065	14.1	31.4	—
11. PET-(PPG-PTMG)	21	2000	0.045	16.5	76.8	—
12. PBT-PPG	21	2000	—	19.9	80.1	—
13. PET-PPG	21	2000	—	20.8	79.2	—

* Calculated from feed ratio

Table 2 Segment ratio analyzed by ¹H-NMR

Block copolymers	Segment Ratio (wt %)			
	Calculated		By ¹ H-NMR	
	polyester	polyether	polyester	polyether
PBT-PTMG (2000)*	21	79	22.3	77.7
PBT-PTMG (2000)	30	70	32.1	67.9
PBT-PEG (2000)	21	79	23.1	76.9
PET-PTMG (2000)	21	79	28.1	71.9
PET-PTMG (1000)	21	79	22.6	77.4
PET-PTMG (1000)	30	70	30.9	69.1

* Molecular weight of polyether used

molecular weight polyether segments, the experimental values are in good agreement with those of calculated values. These block copolymers are expected to have good compositional homogeneity and the segment ratio had been well controlled. In contrast for those multiblock copolymers which have less compositional homogeneity, the experimental values differ appreciably from the calculated.

Mechanical properties

The ultimate properties of the multiblock copolymers have been found to be closely related to $[\eta]$, as shown in Table 3. For PBT-PTMG block copolymer being a thermoplastic elastomer ($[\eta]$ 2.44 dl/g), showed a tensile strength as high as 360 kg/cm² and with 1069% elongation at break. Fig. 4 shows the stress-strain curves of two samples of the same segment composition, one made by monomeric method and the other by the polymeric method, they are rather comparable in behaviour.

Table 3 Ultimate properties

Block copolymers	$[\eta]$ (dl/g)	Tensile strength (kg/cm ²)	Elongation (%)
PBT (21)*-PTMG (2000)**	1.20	200	837
PBT (30)-PTMG (2000)	1.80	312	1065
PBT (30)-PTMG (2000)	2.44	360	1069
PBT (40)-PTMG (2000)	1.73	334	979
PBT (30)-PEG (2000)	1.40	212	852

* wt % of PBT

** MW of polyether

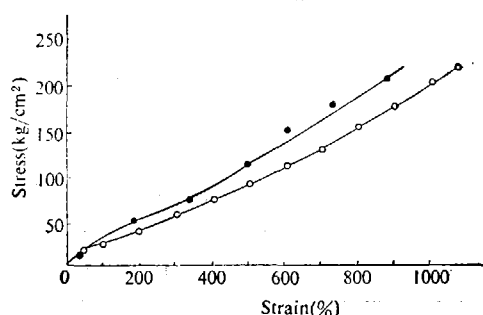


Fig. 4 Stress-strain curves of PBT (21)-PTMG (2000)

—●—Polymeric method;
—○—Monomeric method.

As PBT or PET are commercial available product the polymeric method here described may offer a potential possibility of converting waste commercial polymers to block copolymers of attractive thermoplastic elastomeric properties.

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