

New Block Copolymers II. Synthesis and Characterization of an ABA-Type Block Copolymer

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Synopsis

A new regular ABA-type triblock copolymer has been synthesized by polycondensation of the acid chloride of carboxy-terminated butadiene-acrylonitrile rubber (CTBN) with hydroxy-terminated polyethylene isophthalate (PEI) oligomer. This block copolymer was characterized by elemental (nitrogen) analysis, vapor pressure osmometry, viscometry, and IR and NMR spectroscopy. Quantitative estimation of block segments has been carried out by measuring the area under peaks assigned to various protons in the NMR spectrum of the polymer. NMR spectral analysis has been found to agree well with the nitrogen analysis of the polymer. The solubility and solution viscosity behavior of the polymer has also been studied.

INTRODUCTION

Studies on ABA-type block copolymers are of great interest recently.¹⁻⁹ Synthesis of block copolymers containing polyester segments is commercially attractive in order to improve the properties of conventional polyesters. The ABA type of block copolymer consists of two segments of different chemical natures, one of which serves as a hard segment and the other as a soft segment in the macrochain. This is expected to give rise to unique material by simultaneously overcoming the processing and/or performance deficiency of the individual segment polymer.

There are various methods for the synthesis of ABA-type block copolymers.^{6,10-14} Synthesis of ABA-type block copolymer could be achieved¹⁵ by (1) direct condensation of 2 mol of the bifunctional A prepolymer with 1 mol of the difunctional B prepolymer, (2) reacting 2 mol of the monofunctional A segment having an unreactive group in the other end with 1 mol of the bifunctional B cosegment, (3) using protecting groups to protect one reactive group of a bifunctional A, when its 2 mol are used with 1 mol of the bifunctional B, and (4) miscellaneous specific methods. Recently, direct condensation of 1 mol of a difunctional acid chloride-terminated prepolymer [poly(*m*-phenylene isophthalamide)] with more than 2 mol of a hydroxy-terminated prepolymer (polyethylene oxide) has been successfully demonstrated by a group of workers.¹⁴

In this communication we report synthesis of a new ABA-type block copolymer by reacting hydroxy-terminated polyethylene isophthalate (PEI) with carboxy-terminated butadiene-acrylonitrile low-molecular-weight liquid rubber. Recently we have studied a new (*A-B*)_n-type block copolymer¹⁶ by reacting the acid chloride-terminated polyester with the amine-terminated nitrile rubber.

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EXPERIMENTAL

Reagents

The isophthalic acid (E. Merck, India) used was of pure grade. Ethylene glycol (BDH, reagent grade) was purified by refluxing over anhydrous sodium sulfate and subsequent distillation under reduced pressure.

N,N-dimethylformamide (E. Merck, India) was kept over anhydrous MgSO_4 for 24 h and then distilled under reduced pressure (~ 20 torr). Benzene and *n*-hexane were purified by the usual procedure. All other solvents used were of pure grade.

Thionyl chloride (S.D., India) and triethylamine were freshly distilled after proper treatment.

Carboxy-terminated butadiene-acrylonitrile rubber (Hycar, CTBN) was obtained from B. F. Goodrich Chemical Company and was used without further purification. It has the following specifications: molecular weight, 3320; equivalent per 100 g of rubber (EPhR), 0.057.

Prepolymers

Preparation of Polyethylene Isophthalate (PEI)

In a reaction flask fitted with a distillation setup and a thermometer, 10 g (0.068 mol) of isophthalic acid and 8.43 g (0.136 mol) ethylene glycol were taken. The reaction mixture was heated at 160°C for 1 h under vacuum before heating was started. Then it was heated further for 1 h at 210°C until all the acid was dissolved and a colorless viscous liquid was found. The prepolymer formed was dissolved in DMF and precipitated in water. The white polyester was filtered, washed with 5% sodium bicarbonate solution, finally with water and methanol, and dried. The yield of the prepolymer was 90%.

Determination of Hydroxy Equivalent of PEI

The procedure was as follows. About 4 g PEI was dissolved in 20 mL of reagent-grade dimethylsulfoxide solvent in a 500-mL conical flask. Then 10 mL of acetylating agent ($68.85 \times N$ mL of acetic anhydride in 250 mL pyridine, where normality of the methanolic NaOH $N = 0.39$) and 10 mL of pyridine were added to the titration vessel successively. The whole mixture was then stirred at 60°C for 2 h. After adding 20 mL of *n*-butanol with 50 mL of water, the reaction mixture was cooled and titrated with 0.39 *N* methanolic NaOH solution using mixed indicator (one part of 0.1% aqueous cresol red indicator to three parts of 0.1% aqueous thymol blue indicator). An exactly similar titration for blank was carried out. Thus the hydroxy equivalent of the PEI sample was calculated as follows.

$$\text{Hydroxy equivalent} = \frac{N (\text{titer blank} - \text{titer sample})}{\text{sample weight}} = 1.05$$

Using this hydroxy equivalent value the number-average molecular weight (Table I) of the polyester was found.¹⁷

TABLE I
Physical Properties and Characterization of ABA Triblock Copolymer

Polyester (PEI)		CTBN rubber	ABA copolymer		Inherent viscosity at 30°C (dL/g)		%CTBN ^a rubber	% Nitrogen	
M_n^a	M_n^b	M_w	M_n^c	Density (g/cm ³)	Melting Point (°C)	PEI	ABA copolymer	Calculated ^e	Found
2000	1940	3320	7900	1.02	90	0.09	0.31	1.90	1.89

^a Obtained from ¹H-NMR spectrum of PEI.

^b Obtained from end-group analysis.

^c Measured from vapor pressure osmometry.

^d Weight percentage of CTBN rubber from ¹H-NMR analysis.

^e Theoretical percentage of nitrogen obtained from eq. (5).

Preparation of Acid Chloride Derivative of CTBN

In a reaction flask, 3 g (0.0009 mol) of CTBN was dissolved in 25 mL benzene. Thionyl chloride, 1 mL, was added to it and was refluxed for 24 h at 90° C. Next, excess benzene and thionyl chloride were removed by rotary evaporator and finally washed with dry *n*-hexane and dried under vacuum.

Polymer Synthesis

The block copolymer was prepared by reacting the hydroxy-terminated prepolymer (PEI) with the acid chloride derivative of CTBN at a low temperature in the presence of an acid acceptor.

Synthesis of Polymer from PEI and CTBN

In a 250-mL reaction flask fitted with a Teflon stirrer, a thermometer, and a dropping funnel, 3.6 g (0.0018 mol) of hydroxy-terminated polyethylene isophthalate prepolymer was dissolved in 10 mL of dry DMF. The acid chloride of CTBN (0.0009 mol) dissolved in 20 mL DMF was added to the PEI prepolymer at 0° C. After 1 h, triethylamine was added to the reaction mixture followed by an addition of ~1% (based on CTBN) antioxidant (*N*-isopropyl *N'*-phenylphenylenediamine). The mixture was stirred for 4–5 h at 60° C to ensure completion of the reaction. The reaction mixture was poured in ice water with vigorous stirring, and the polymer obtained as a precipitate was filtered.

Purification of the Polymer

The polymer obtained after filtration was put into a mixture of benzene and *n*-hexane (3:2 by volume), the mixture was stirred for a few minutes, and the supernatant liquid was decanted off. The polymer was dissolved in dioxane and reprecipitated in cold water containing sodium chloride, filtered, washed with *n*-hexane, and dried in vacuum at room temperature. The yield of the polymer was about 80%.

Polymer Characterization

Viscosity Measurement

Viscosity measurements were performed in 0.5% (*w/v*) solutions of polyester and copolymer in *N*-methyl-2-pyrrolidone at 30° C using a Ubbelohde suspended-level viscometer.

Solubility Characteristics

Block copolymer was placed in 2 mL of various solvents and kept for 2 weeks. Then the swelling or dissolution of the copolymer was carefully judged.

IR Spectroscopy

Infrared, (IR) spectra were recorded by a Perkin-Elmer 237B spectrophotometer using nujol mull. Chloroform was also used in case of acid chloride of CTBN.

¹H-NMR Spectroscopy

The ¹H-NMR spectra of the polyester and the copolymer were recorded by a Varian EM-390 type 90 MHz spectrometer using DMSO-*d*₆ as solvent and TMS as standard.

Molecular Weight of the Copolymer

The molecular weight of the copolymer was obtained on a Knauer Dampf Druck vapor pressure osmometer after calibration with benzil using dioxane solvent at 60° C.

RESULTS AND DISCUSSION

The condensation between the PEI and the acid chloride of CTBN rubber was carried out at low temperature in the presence of triethylamine as acid acceptor. The overall reaction scheme for the synthesis of copolymer is shown in Figure 1. No catalyst was used in these polymerization reactions.

Polymer Characterization

The block copolymer was characterized by IR and ¹H-NMR spectroscopy, nitrogen analysis, and molecular weight determination by vapor pressure osmometry and viscometry.

The IR Analysis of ABA Block Copolymer

IR spectrum of the copolymer is shown in Figure 2. The IR spectrum shows the characteristic absorption band at 1725 cm⁻¹ due to carbonyl stretching vibration of the ester group in the polyester segment. The infrared absorption band with low intensity was found at 1620 cm⁻¹, which is assigned to the double bonds in the parent CTBN cosegment, and, the

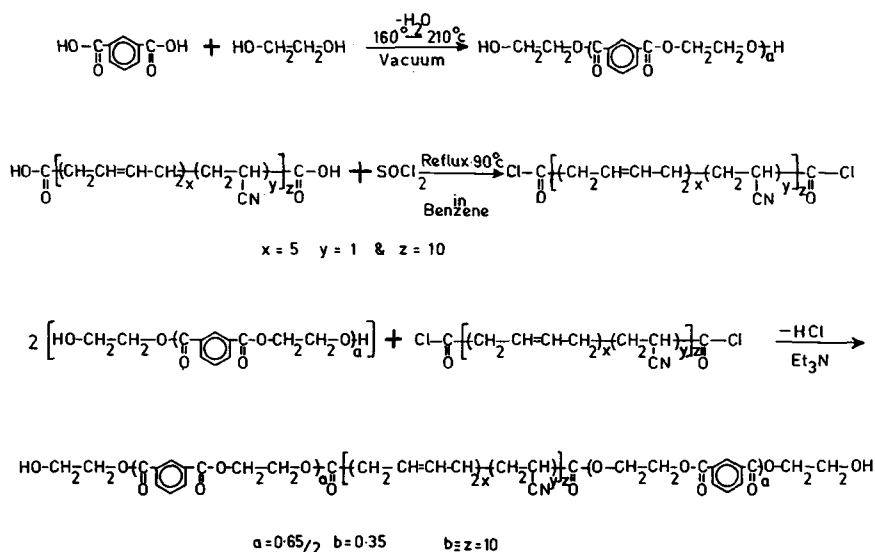


Fig. 1. Scheme for the synthesis of ABA block copolymer.

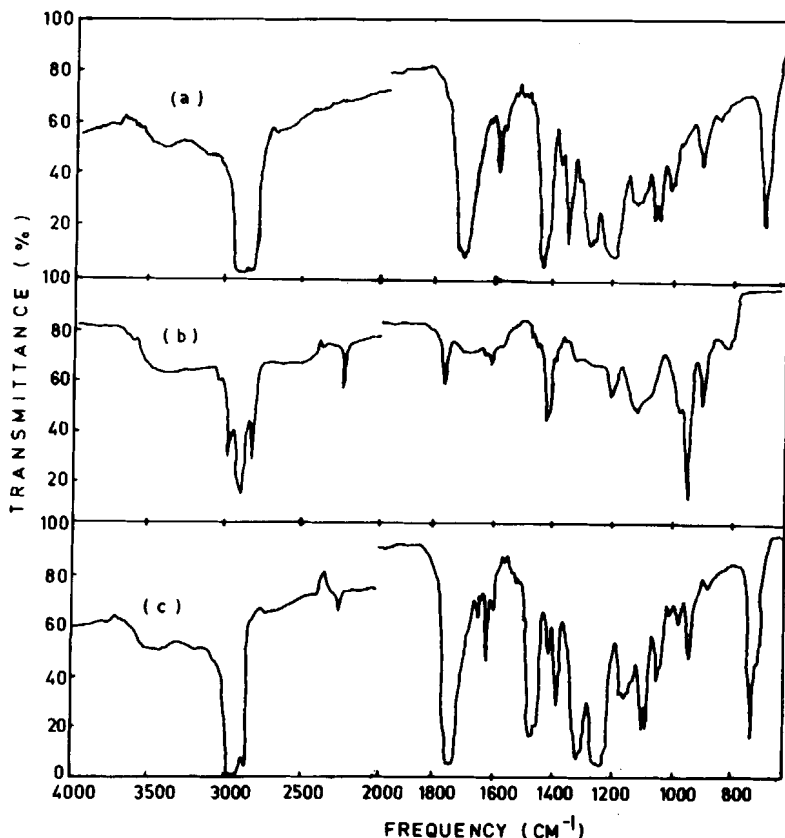


Fig. 2. IR spectra of the polymers: (a) polyethylene isophthalate (PEI); (b) acid chloride of CTBN rubber; (c) ABA block copolymer.

$C\equiv N$ band appeared in the region $2240\text{--}2250\text{ cm}^{-1}$. A broad-band assignable to the $-OH$ groups at the terminal of the copolymer molecule was also observed in the $3300\text{--}3400\text{ cm}^{-1}$ region. The characteristic peak at 1600 cm^{-1} found in the IR spectrum of the homopolymer (polyester) was also observed in the block copolymer. Thus the infrared spectroscopy confirms the presence of both polyester and CTBN segments in the copolymer (Fig. 2).

1H -NMR Analysis of ABA Block Copolymers

The 1H -NMR spectrum of the copolymer is shown in Figure 3. A sharp singlet at $\delta 8.35$, a broad singlet at $\delta 8.00$, and a multiplet at $\delta 7.5$ are due to three kinds of aromatic protons a' , b' and c' respectively. A singlet peak of very low intensity at $\delta 4.9$ may be due to $-OH$ protons in the terminal of copolymer molecule. Another sharp singlet was found at $\delta 4.5\text{--}4.6$ due to $-O-CH_2-CH_2-O-$ protons, and a unresolved symmetrical triplet was found at $\delta 4.3$ due to $-CH_2CH_2OH$ protons in the terminal of copolymer molecule. A similar type of peak due to $-CH_2OH$ protons was found at $\delta 3.7\text{--}3.8$. The weaker signals present at $\delta 5.3$ and $\delta 2.65$ are due to $-CH=CH-$ and $-CH-$ protons, respectively, in the copolymer chain.



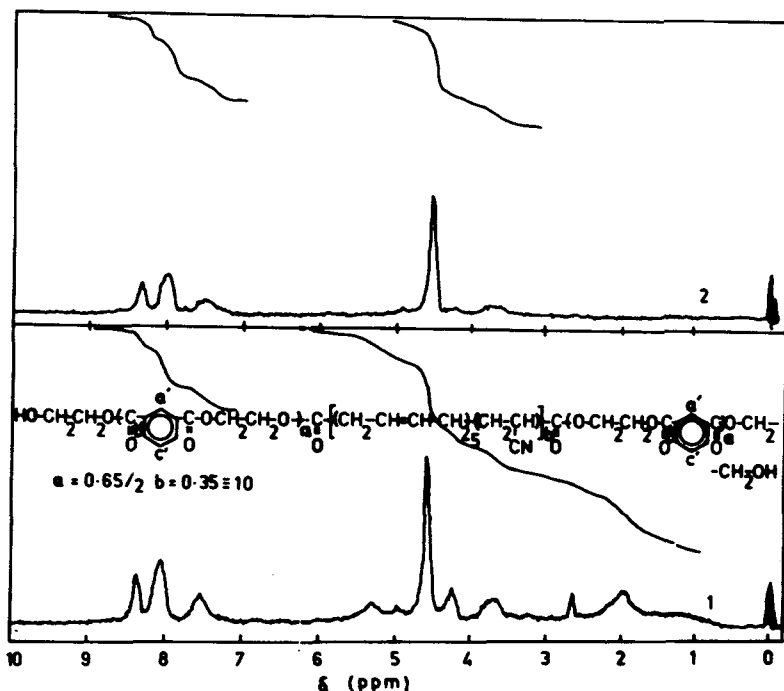


Fig. 3. $^1\text{H-NMR}$ spectra of the polymers: (1) ABA block copolymer; (2) polyethylene isophthalate (PEI).

All the other CH_2 protons in the monomer unit of CTBN, the internal unit or cosegment in the ABA type of block copolymer, come under the broad signal in the region $\delta 1.0\text{--}2.48$. So it seems clear from the appearance of various characteristic peaks in the $^1\text{H-NMR}$ spectrum of the copolymer that incorporation of CTBN has been achieved in the macrochain.

Copolymer Composition from $^1\text{H-NMR}$ Analysis

For quantitative estimation of the amount of CTBN incorporated in the copolymer, $^1\text{H-NMR}$ spectroscopy has been utilized. The areas under respective peaks in the $^1\text{H-NMR}$ spectrum assigned to protons of both segments, polyester and CTBN, have been calculated. A distinctive peak, although with very low intensity, for two hydroxy protons at $\delta 4.9$ in the $^1\text{H-NMR}$ spectrum of the polyester (Fig. 3), has been used as an internal standard for the determination of its molecular weight. The block composition of the copolymer has been computed from the ratio of peak areas of two segments.

Ratio of the total areas under two segments

$$= \frac{\text{total area under PEI segment (A)}}{\text{total area under CTBN segment (B)}} = 1.8 \quad (1)$$

Repeat unit of CTBN segment in copolymer

$$= \frac{B}{A + B} \times 100\% = 35\% \quad (2)$$

Repeat unit of segment in copolymer

$$= \frac{A}{A + B} \times 100 = 65\% \quad (3)$$

Representing the copolymer structure as $(PEI)_a - (CTBN)_b - (PEI)_a$, we get the repeat unit ratio of polyester and CTBN:

$$2a/b = 1.8 \quad (4)$$

where $2a = 0.65$ and $b = 0.35$ obtained from eqs. (3) and (2), respectively. According to the resolution observed for CTBN and PEI homopolymers in the proton NMR spectrum of the copolymer, eq. (4) is reasonable. The value of $b = 10$ is available from the specification of CTBN. Therefore, from eq. (4) we get $a = 9$. The weight percentage of CTBN block present in the copolymer may be calculated as

$$\%CTBN = \frac{0.35 \times M_2}{0.65 \times M_1 + 0.35 \times M_2} \times 100\% = 47\% \quad (5)$$

where $M_1 = 192$ and $M_2 = 323$ are the molecular weights of polyester and CTBN repeat unit, respectively.

This $^1\text{H-NMR}$ spectral analysis may also be used for the determination of sequence distribution in copolymer chain, although it has some limitations because of inadequate resolution¹⁸ of the spectrum for the parent homopolymers. The copolymer composition data correspond well with those of nitrogen (elemental) analysis. The theoretical percentage of nitrogen calculated from eq. (5) agrees with the experimental value of nitrogen analysis (Table I). Further support of the ABA structure of the copolymer comes from the molecular weight determination of copolymer by vapor pressure osmometry (Table I).

Polymer Properties

Solubility Characteristics

Solubility of the prepolymer components and the block copolymer in different solvents is given in Table II. The copolymer is highly soluble in polar solvents, which can be explained by the fact that the presence of polar groups makes the polymer soluble in dipolar aprotic solvents due to dipole-dipole interaction.^{19,20} From the solubility behavior (Table II), it is again very clear that the synthesized copolymer is similar in behavior to both the parent prepolymers.

Solution Viscosity Behavior

The inherent viscosities of the copolymer and the polyester are shown in Table I. The viscosity value in the case of the copolymer is about three times greater than that of polyester.

TABLE II
Solubility Characteristics of the Parent Prepolymers and the Block Copolymer

Solvents	Polyester ^a	CTBN ^a	ABA copolymer ^a
Acetone	-	-	-
Ethyl methyl ketone	-	+	±
Benzene	-	+	±
Toluene	-	+	±
Tetrahydrofuran	-	+	±
Methylene dichloride	-	+	±
Chloroform	-	+	±
Chlorobenzene	-	+	±
Nitrobenzene	-	+	±
<i>n</i> -Hexane	-	-	-
<i>N,N</i> -Dimethylformamide	+	+	+
Dimethylsulfoxide	+	+	+
<i>N</i> -Methyl-2-pyrrolidone	+	+	+
1,4-Dioxane	-	+	+
<i>m</i> -Cresol	+	+	+
Cyclohexanone	-	-	-

^a Solubility: +, soluble; ±, swelling or partly soluble; -, insoluble

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