

New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Initiator-Transfer Agents (Inifers)*

21. Synthesis and Characterization of A Block Copolymer of Polyisobutylene and Poly(Bisphenol A Carbonate)

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SUMMARY

A new alternating block copolymer consisting of polyisobutylene and poly(bisphenol A carbonate) has been prepared and characterized. The synthesis involved coupling of α, ω -di(hydroxy)polyisobutylene and phenol terminated poly(bisphenol A carbonate) by hexamethylene-1,6-diisocyanate. According to GPC measurement the \bar{M}_n of the block copolymer has increased ~ 2.5 times of the sum of prepolymers. Evidence for blocking was also obtained by IR spectroscopy. The volume ratio of soft segment, polyisobutylene, to hard segment, poly(bisphenol A carbonate), has been determined by NMR spectroscopy. Solution cast films of the block copolymer yielded transparent films which exhibited phase separation by electron microscopy and thermal analysis. Thermal analysis also indicated the presence of crystallinity in this block copolymer.

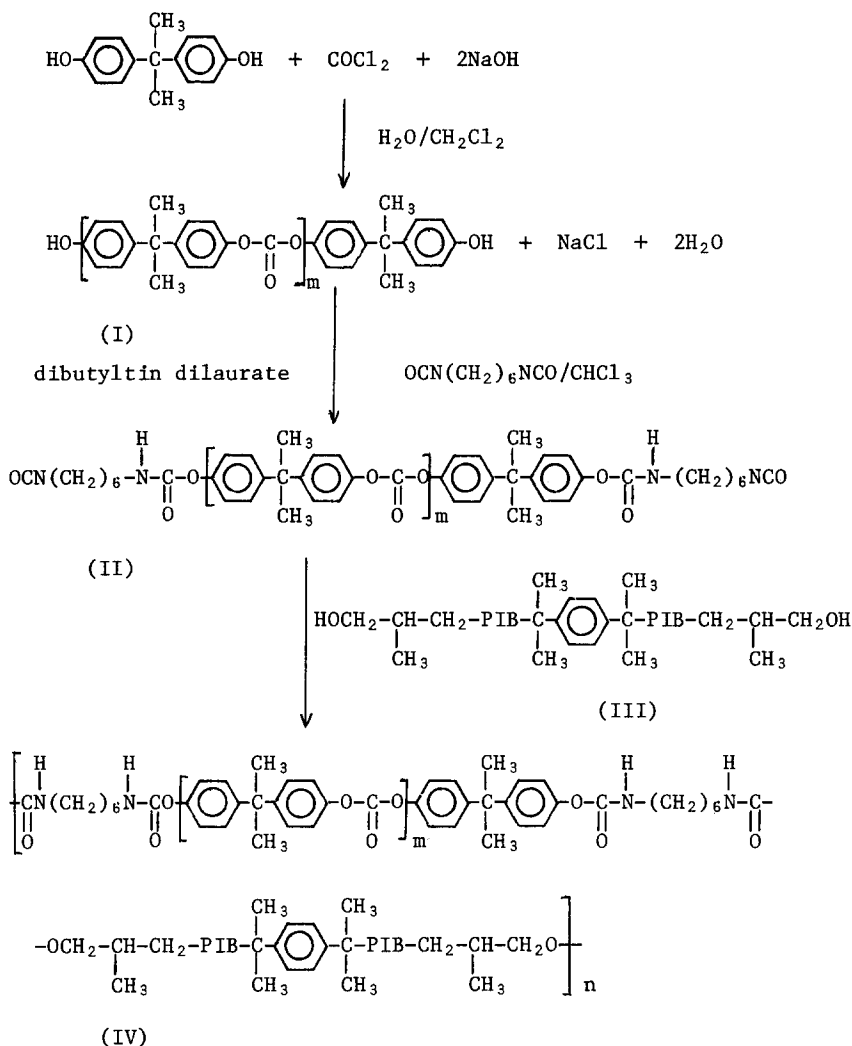
INTRODUCTION

In the course of our continuing investigation on telechelic polyisobutylenes (IVÁN et al., 1980) we have prepared a new polycarbonate block copolymer IV by the route outlined in Scheme 1. Specifically, a rather low molecular weight polycarbonate segment prepared in a conventional manner from bisphenol A (BPA) and phosgene I was "capped" by an excess of hexamethylene-1,6-diisocyanate (HMDI), and the diisocyanate thus obtained II was reacted with hydroxy telechelic polyisobutylene III. This paper describes the synthesis steps involved and the characterization of this new material.

EXPERIMENTAL

A. Materials. The synthesis and purification of hydroxy telechelic polyisobutylene, $\text{HOCH}_2\text{-PIB-CH}_2\text{OH}$ (Formula III in Scheme 1) has been described (IVÁN et al., 1980). The number average molecular weight and terminal functionality of the diol used in this research were $\bar{M}_n = 4,900$ and $F_n = 1.95 \pm 0.07$, respectively. Phosgene (Matheson), HMDI (Aldrich), methylene chloride (Fisher), and dibutyltin dilaurate (Polyscience) were used directly without further purification. BPA (Aldrich) was recrystallized from toluene. Chloroform (Fisher) was washed with water, dried over calcium chloride, and further purified

Scheme 1. Synthesis of Isobutylene-Bisphenol A Carbonate Block Copolymer



by distillation from phosphorus pentoxide.

B. Polymerizations. The linear aromatic polycarbonate derived from BPA was prepared by interfacial condensation of phosgene and BPA in the presence of excess alkali and water, and methylene chloride as immiscible solvents. A detailed synthetic procedure and characterization of poly(BPA carbonate) has been described by MERRILL (1961).

Subsequently, 0.667 g (0.333 m mole) poly(BPA carbonate) was reacted with 0.112 g (0.667 m mole) HMDI in the presence of

0.03 g (0.05 m mole) dibutyltin dilaurate catalyst in 25 ml chloroform. The charge was stirred and refluxed under N_2 for five hours; then 1.630 g (0.33 m mole) of $HOCH_2-PIB-CH_2OH$ in 25 ml $CHCl_3$ was added and stirring was continued overnight. The product was extracted with hexanes (Aldrich) to remove unreacted $HOCH_2-PIB-CH_2OH$. Efforts to remove unreacted isocyanate-capped poly(BPA carbonate) (Formula II in Scheme 1) by solvent fractionation techniques failed. The hexanes-insoluble fraction was completely soluble in pyridine although even very low molecular weight PIB is insoluble in this solvent. Evidently, the pyridine-soluble carbamate and aromatic groups pull the PIB segments into solution. Thus the hexanes-insoluble fraction was regarded the sought block copolymer. Block copolymer films obtained by casting chloroform solutions (chloroform is a good solvent for all constituents) were optically clear.

C. Instrumentation. Gel permeation chromatography was carried out using a Waters Associates 6000A high pressure GPC pump, dual UV & RI detectors, and Microstyrigel columns of 10^6 , 10^5 , 10^4 , 10^3 , 500Å pore size. Sample concentration was 0.25-0.30% in THF, and the flow rate was 2 ml/min.

1H NMR analysis was carried out by using a Varian Associates T-60 NMR spectrophotometer. Solutions of ~10% polymer in $DCCl_3$ were employed. Infrared spectra were recorded on a Perkin-Elmer 521 Grating IR spectrophotometer using polymer films.

Scanning electron micrographs were taken on a JSM-U3 Scanning Electron Microscope, SEM(JEOL). For SEM studies, films of block copolymers or polyblends (obtained by mixing PIB and poly(BPA carbonate) in $HCCl_3$, were cast directly on polished SEM stubs which were then vacuum coated with a thin layer of gold.

Differential scanning calorimetry was carried out in the heating mode with a DuPont 990 Differential Scanning Calorimeter using ~20mg samples and 20°C/min heating rate. Immediately before scanning the samples were cooled to -120°C. A nitrogen atmosphere was provided by flushing the dried gas through the sample holder at a constant rate of 30 cm^3min^{-1} . The low-temperature device filled with liquid nitrogen was used for measurements of low transition temperatures. The temperature scale of the instrument was calibrated by determining the m.p. of Hq (-38.9°C) and In (156.6°C).

RESULTS AND DISCUSSION

The synthesis principle is outlined in Scheme 1. Figure 1 shows the GPC traces of the polycarbonate (I in Scheme 1), the $HOCH_2-PIB-CH_2OH$ (III in Scheme 1), and the final product (IV in Scheme 1). The shift in the position of the GPC trace of the product toward lower elution counts indicates significantly increased molecular weights relative to the starting materials. The pronounced shoulder at ~48 V_e indicates the possible presence of poly(BPA) and diblock copolymer in the final product.

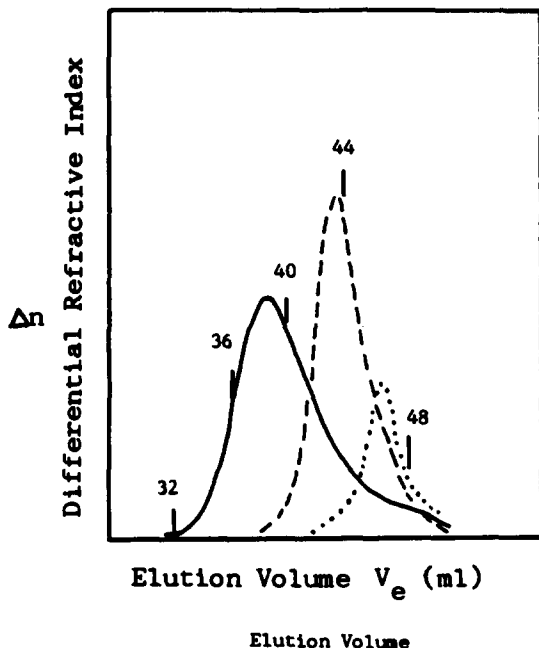


Figure 1: GPC Traces of Isobutylene-BPA Carbonate Block Copolymer (—), PIB diol (---) and PolyBPA Carbonate (...).

Inspection of the infrared spectrum of the final product (Figure 2) also suggests the existence of a block copolymer. The characteristic absorptions of HOCH_2 -termini at 3640 cm^{-1} (dimer), and $\text{HO}-\text{C}_6\text{H}_4$ -termini at 3600 cm^{-1} disappear after coupling and strong peaks associated with the carbamate group appear at 1740 , 3330 , and 3400 cm^{-1} for $\nu\text{C=O}$, $\nu\text{N-H}$ (monomer)

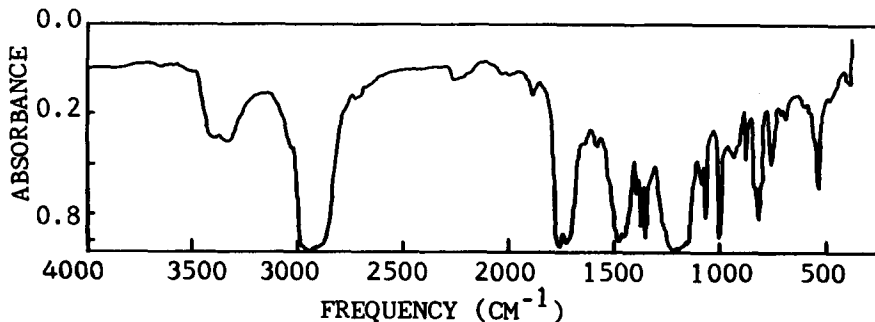


Figure 2: IR Spectrum of Isobutylene-BPA Carbonate Block Copolymer.

and $\nu_{\text{N-H}}$ (dimer), respectively. The major IR absorptions and corresponding structures are shown in Table I.

TABLE I
Infrared Absorption of Isobutylene-BPA Carbonate
Block Copolymer

cm^{-1}	Assignments
830 (w), 880 (w)	p-disubstituted phenyl group
1250 (s)	$-\text{C}(\text{CH}_3)_2-$, skeletal
1360 (s), 1380 (s)	δ_{CH} , gem-dimethyl
1470 (s)	ω_{CH_2}
1740 (s)	$\nu_{\text{C=O}}$ (carbamate)
1770 (s)	$\nu_{\text{C=O}}$ (carbonate)
2270 (w)	ν_{NCO}
2925 (s), 2850 (m)	ν_{CH_2}
2960 (s), 2870 (m)	ν_{CH_3}
3030 (s)	ν_{CH} (arom.)
3330 (m), 3400 (m)	$\nu_{\text{N-H}}$

w = weak, m = medium s = strong

Figure 3 shows the ^1H NMR spectrum of the isobutylene-BPA carbonate block copolymer together with assignments. The methylene protons of HMDI are hidden by the methylene and gem-dimethyl protons of PIB. The protons of the inifer residue are masked by the aromatic protons of BPA. For PIB with $\bar{M}_n = 5,000$, the peak intensity of the four aromatic inifer protons (7.15 ppm) is negligible as compared with the main peaks of methylene and gem-dimethyl protons of PIB. The resonances characteristic of the gem dimethyl groups in BPA and in $\text{HOCH}_2\text{-PIB-CH}_2\text{OH}$, at 1.6 and 1.1 ppm, respectively, can be used for integration and thus to estimate the relative amount (mole) of these constituents in the sample. The ratio of these protons is 0.34, therefore the overall composition of the block copolymer is 61/39 poly(BPA carbonate)/PIB.

Figure 4 shows scanning electron micrographs of a polyblend and a block copolymer. Evidently, poly(BPA carbonate) and PIB are incompatible. Visual and SEM (Figure 4a) examination of fracture surface of blends indicate brittle failure. While very rough surfaces are observed with the polyblend, the block copolymer exhibits much smoother surfaces most likely because the PIB and poly(BPA carbonate) chains in the block copolymer are chemically joined and cannot undergo gross phase

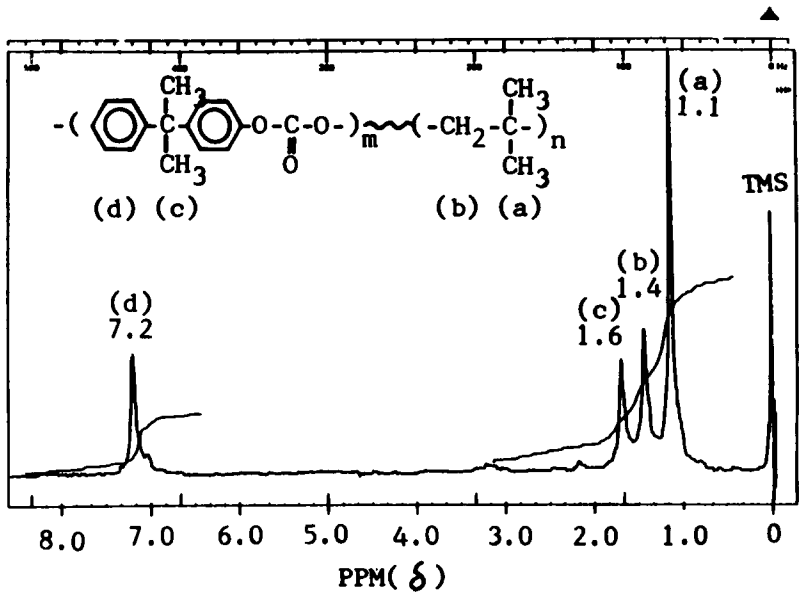


Figure 3: NMR Spectrum (CDCl_3) of Isobutylene-BPA Carbonate Block Copolymer.

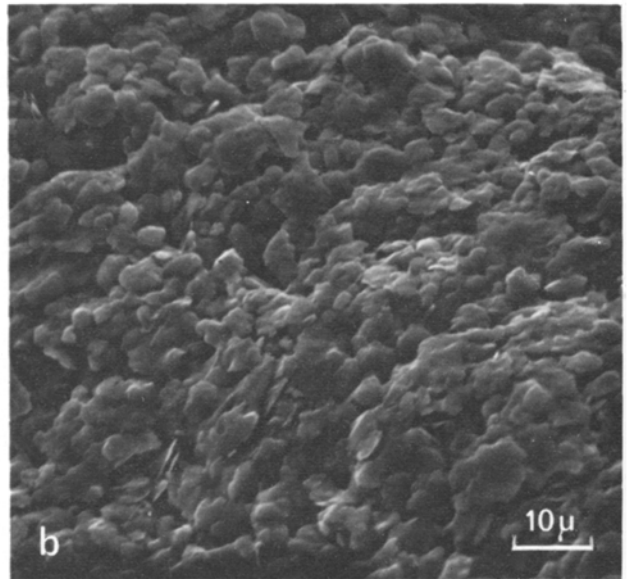
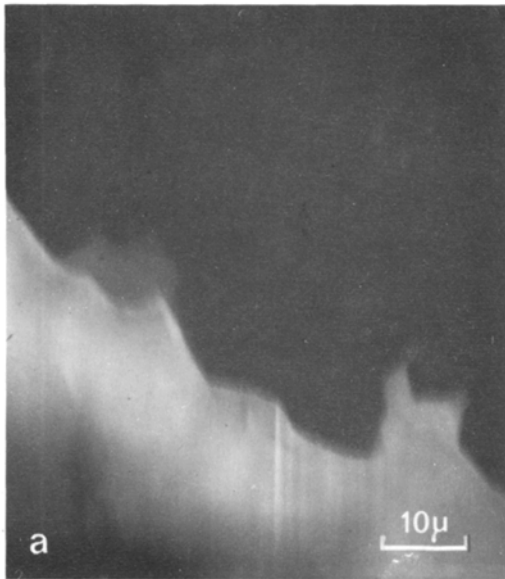


Figure 4: Scanning Electron Micrograph of (a) Polyisobutylene-Poly BPA Carbonate Blend (39/61) (b) Isobutylene-BPA Carbonate Block Copolymer (39/61) Cast from Chloroform (Mutual Solvent).

separation (NOSHAY and MCGRATH, 1977). Based on the overall composition (see above), poly(BPA carbonate) is the continuous phase and PIB is the dispersed phase.

Microphase separation is also indicated by DSC analysis. Figure 5 shows DSC traces of the component homopolymers and the block copolymer. The T_g of HOCH₂-PIB-CH₂OH appears at -75°C whereas that of the poly(BPA carbonate) at 79°C. Poly(BPA carbonate) recrystallized from CH₂Cl₂ shows an endotherm at 132°C; Poly(BPA carbonate) recrystallized from CH₂Cl₂ shows an endotherm at 132°C;

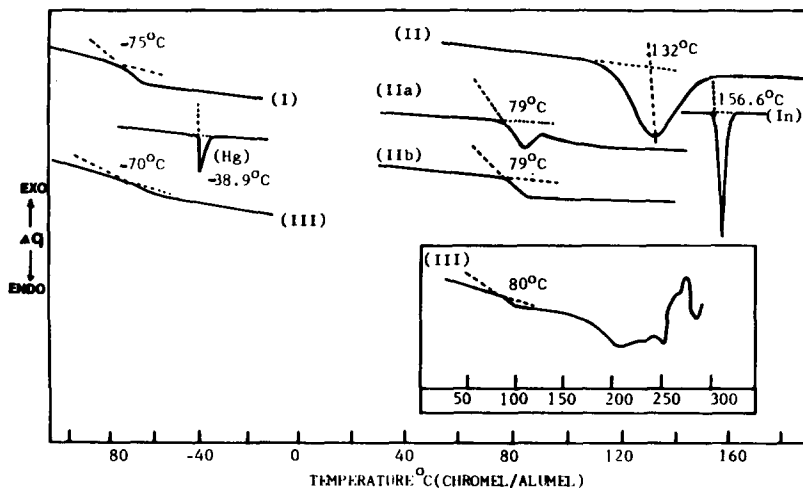


Figure 5: DSC Traces of HO Terminated PIB(I), PolyBPA Carbonate Crystallized from CH₂Cl₂ (II), quenched by air (IIa), (IIa quenched by liq. N₂ (IIb) and Isobutylene-BPA Carbonate Block Copolymer (III) (Heating rate 20°C/min.)

when a melt of this material is cooled in air (1°C/min) or is rapidly quenched in liquid nitrogen, it exhibits transitions at 79°C (curves II, IIa and IIb). According to WOLPERT et al., (1971), poly(BPA carbonate) shows a strong endotherm at 79°C upon heating samples annealed above the T_g . The isobutylene BPA carbonate block copolymer exhibited a T_g at -70°C characteristic of PIB and one at 80°C associated with the poly(BPA carbonate) segment (curve III). The ~5°C higher T_g of the PIB segment as compared to the homopolymer may be due to immobilization of chain ends. The endotherms in the range from 175 to 275°C in the block copolymer suggest a measure of crystallinity and strong H-bridges between the N-H of the carbamate and C=O of the carbonate groups.

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