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Macromers by Carbocationic Polymerization. X. Synthesis, Characterization, and Polymerizability of Cyanoacrylate-Capped Polyisobutylenes

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MACROMERS BY CARBOCATIONIC POLYMERIZATION. X.† SYNTHESIS, CHARACTERIZATION, AND POLYMERIZABILITY OF CYANOACRYLATE-CAPPED POLYISOBUTYLENES

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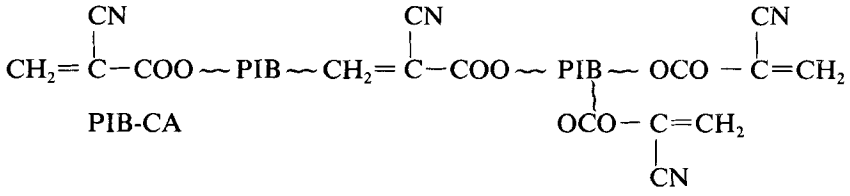
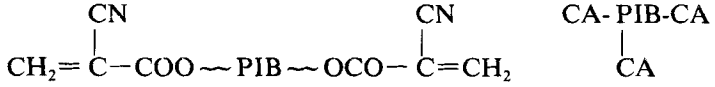
ABSTRACT

The objectives of this research were the synthesis and characterization of the following linear and three-arm star cyanoacrylate polyisobutylenes:



PIB-CA



CA-PIB-CA

CA-PIB-CA

†For Part IX, a preliminary report on this subject, see *Polym. Prepr., 31*(2), 655 (1990).

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and an examination of their polymerizability. The syntheses involved the Diels–Alder protection of 2-cyanoisobutyl acrylate (IB-CA) with anthracene followed by hydrolysis and conversion to the 2-cyanoacryloyl chloride. The protected cyanoacryloyl chloride was then reacted with one- or two-ended linear or three-ended three-arm star $-CH_2OH$ terminated polyisobutylenes (PIB-OH, HO-PIB-OH, and HO-PIB-OH / OH). Deprotection by excess maleic anhydride yielded the target macromers. ^{1}H-NMR and FTIR spectroscopic analyses indicated quantitative $CH_2=C(CN)COO-$ end-capping. The solution polymerization of a PIB-CA macromer ($\overline{M}_n$ = 2380) with *N,N*-dimethyl-*p*-toluidine (DMT) at room temperature gave high molecular weight product ($\overline{M}_n \approx 35{,}000$). Solution polymerization of CA-PIB-CA and CA-PIB-CA / CA gave networks with low (9–12%) sol fractions. The bulk copolymerization of CA-PIB-CA / CA with IB-CA also occurred readily.

INTRODUCTION

Terminally functional polymers are of great scientific and commercial importance [1]. Recently convenient methods have been developed in our laboratories for the synthesis of linear and three-arm star polyisobutylenes (PIBs) carrying one, two, and three primary alcohol ($-CH_2OH$) end-groups [2]. These prepolymers can be quantitatively derivatized; for example, to acrylate telechelic PIBs [4, 5].

2-Cyanoalkyl acrylates (e.g., methyl, ethyl, isobutyl, etc.) are highly reactive monomers and undergo rapid polymerization even in the presence of mild initiators, such as H_2O, amines, etc. [6, 7]. The objectives of this research were the synthesis and characterization of linear and three-arm star PIBs carrying cyanoacrylate end-groups and an examination of the polymerizability of these terminally-functional PIBs.

EXPERIMENTAL

Materials

The synthesis and purification of HO-capped PIBs have been described [2]. Benzene, hexanes, methylene chloride, triethylamine, and *p*-xylene were distilled over CaH_2 under a N_2 atmosphere. 2-Cyanoisobu-

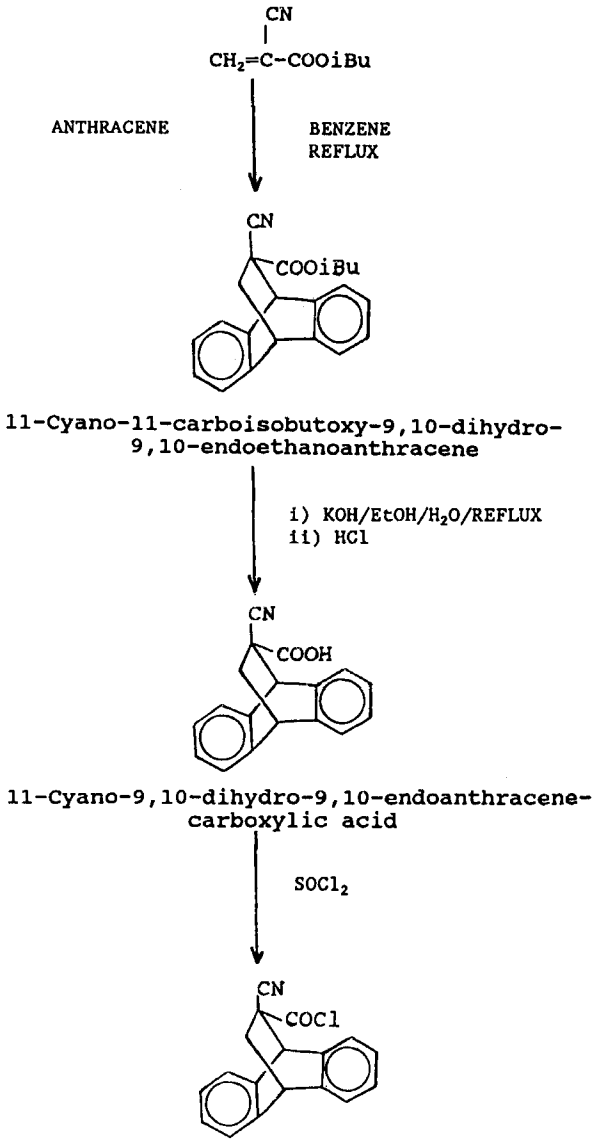
tyl acrylate (IB-CA) (Sigma), anhydrous SO_2 (Matheson), anthracene, maleic anhydride, *N,N*-dimethyl-*p*-toluidine (DMT) (Aldrich), and thionyl chloride (Fisher) were used as received. Reagent grade THF, nitromethane, and hexanes were used for swelling and extraction studies.

Synthesis and Characterization

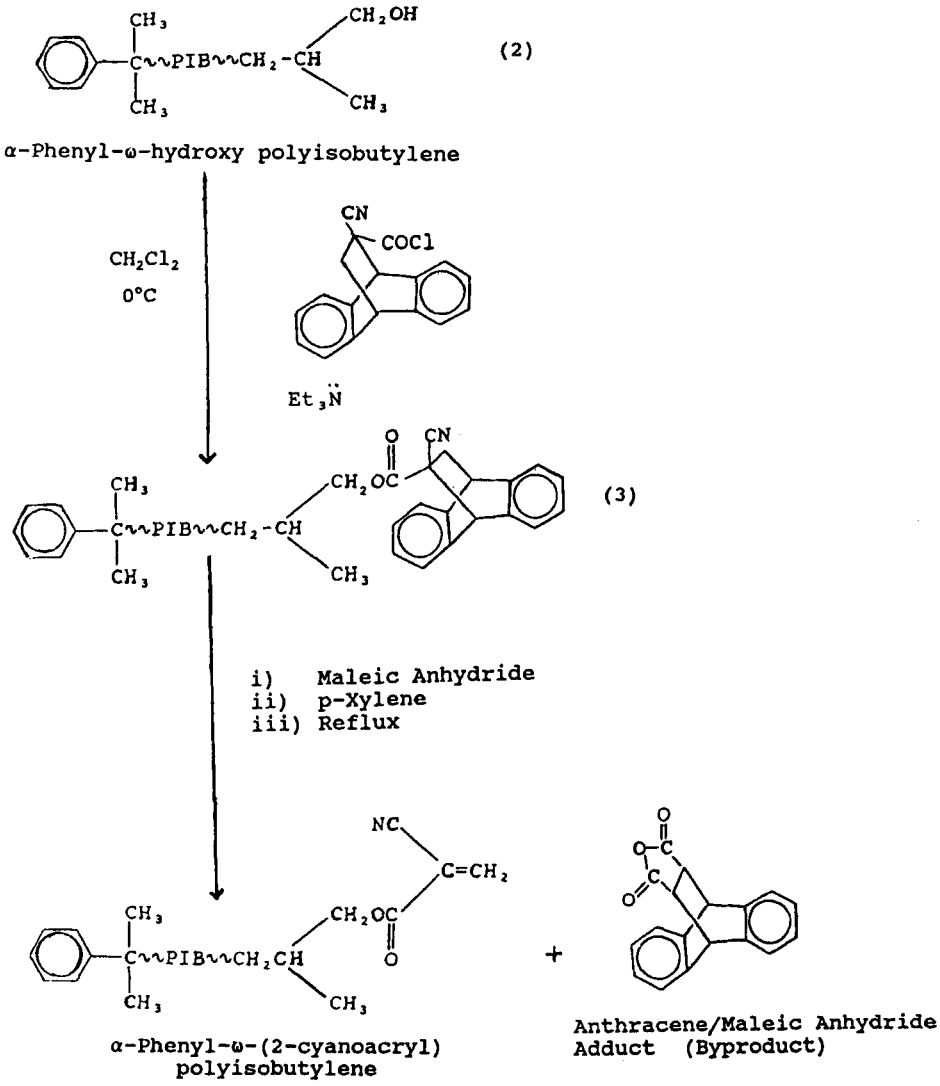
The synthesis of narrow molecular weight distribution (MWD) linear and three-arm star PIBs carrying *tert*-chlorine end-groups was carried out by living carbocationic polymerization [8], followed by quantitative dehydrochlorination and hydroboration/oxidation to $-CH_2OH$ groups [2]. The synthesis of protected 2-cyanoacryloyl chloride was carried out according to Scheme 1. The yields for the products in Scheme 1 were essentially the same (80–90%) as those in the references [9, 10]. Scheme 2 outlines the esterification of PIB-alcohols by the protected cyanoacryloyl chloride and deprotection to give the sought products. While Scheme 2 outlines the strategy for the synthesis of only PIB-CA, the same procedure has also been followed to prepare CA-PIB-CA and  except, in these instances, PIB diols and triols were employed.

Esterification of the PIB-alcohols was carried out by the procedure of Kennedy and Hiza [4, 5]. Thus, a solution of PIB-OH (2 in Scheme 2) in dry CH_2Cl_2 and triethyl amine (twofold mole excess based on cyanoacryloyl chloride) was added to a solution of protected cyanoacryloyl chloride (twofold excess on $-CH_2OH$ groups) in CH_2Cl_2 at 0°C. After stirring overnight at room temperature, the mixture was filtered and the triethylamine and CH_2Cl_2 were evaporated. The pure product (3 in Scheme 2) was obtained by column chromatography on neutral alumina (activity 1) using a mixture of hexanes and CH_2Cl_2 as eluent.

The displacement of the protecting group was carried out by heating the polymer in an inert solvent in the presence of a more reactive dienophile, i.e., maleic anhydride. Thus, to a solution of 3 in dry *p*-xylene (SO_2 inhibited) was added maleic anhydride (5 mol% excess relative to end-groups), a trace of P_2O_5 and hydroquinone (inhibitor). The mixture was refluxed for 15 h at 140°C, cooled to room temperature, and the anthracene/maleic anhydride by-product filtered off. The solvent was removed at 35–40°C under reduced pressure, the crude product dissolved in dry hexanes, and filtered to remove excess maleic anhydride and residual crystalline anthracene/maleic anhydride adduct. The residual xylene was removed by repeated addition and evacuation of hexanes to yield



SCHEME 1.



SCHEME 2.

the pure PIB-CA. The functionalized polymer was freeze-dried to remove the last traces of solvents. The yields were essentially quantitative for both the esterification of the PIB-alcohols and the deprotection. Minor polymer losses during work-up was unavoidable.

The structure of the polymers was analyzed by ^{1}H-NMR (Varian Gemini-200 instrument) and FTIR (Beckman FT100 spectrometer) spectroscopies. Molecular weights were determined by GPC (Waters high pressure instrument, Model 6000A pump) using a series of μ-styragel columns (100, 500, 10^3, 10^4, 10^5 Å), a differential refractometer (Model 410), and a Wisp (710B) automatic sampler. The flow rate was 1 mL THF/min. The calibration curves were obtained with narrow MWD PIB standards. Details of these analytical techniques have been described [1, 3].

Homopolymerization and Copolymerization of Telechelics

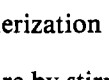
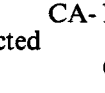
Polymerizations were conducted in large (~75 mL) test tubes in a stainless steel dry box under dry N_2. Homopolymerizations of PIB-CA, CA-PIB-CA and  were carried out in the presence of DMT. Details of the charges (starting materials and concentrations) are given in Table 1. In the case of CA-PIB-CA and  , the charge was poured into a Teflon mold (3 × 3 × 0.5 cm) and stored at room temperature under a blanket of dry N_2 for 2 days to obtain a film. The percent soluble (sol) fractions were determined by extraction of three samples of each polymer with THF, a good solvent for these telechelics. Thus, three preweighed samples were immersed in THF at room temperature, and the swollen samples were blot dried and weighed every 24 h until weight constancy was reached. Then the samples were dried in a vacuum oven at ambient temperature to constant weight and the sol fractions were determined. The copolymerization of  and IB-CA was carried out at room temperature by stirring the charge with a wood applicator soak-dried with DMT [17], pouring it into a Teflon mold, and curing at room temperature in a dry box under nitrogen for 2 days. The unreacted  was removed by extraction with THF,

TABLE 1. Representative Macromers and Extraction Data

	Prepolymer			Network, sol fraction, %[b]
	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{F}_n$[a]	
1. PIB-CA	2380	1.16	0.9 ± 0.05	–
2. CA-PIB-CA	1500	1.54	1.90 ± 0.1	–
3. CA-PIB-CA[c]	1390	1.20	1.90 ± 0.1	9.0
4. CA-PIB-CA[c] (CA)	2080	1.16	2.93 ± 0.15	9.6
5. CA-PIB-CA/IB-CA[d] (CA)	2080/153.1	1.16/1.0	2.93/1.0	12.0

[a]By ^{1}H-NMR.

[b]Average of three extractions.

[c][CA-PIB-CA] = 0.025 *M*; [DMT] = 0.005; in benzene. For conditions, see Experimental section.

[d]Copolymer composition 9/91 mol% (30/70 wt%); CA-PIB-CA/IB-CA (CA). For conditions, see Experimental section.

and the poly(IB-CA) was removed by extraction with nitromethane by using the extraction procedure described above.

RESULTS AND DISCUSSION

A) Synthesis and Characterization

Schemes 1 and 2 show the steps involved in the synthesis of linear monofunctional cyanoacrylate-capped macromer (PIB-CA). The bifunctional linear (CA-PIB-CA) and trifunctional three-arm star $\left(\begin{array}{c}\text{CA-PIB-CA}\\ \quad\quad|\\ \quad\text{CA}\end{array}\right)$ telechelic macromers have been obtained by the same strategy except that the linear PIB glycol HO-PIB-OH and the tri-arm star triol $\begin{array}{c}\text{HO-PIB-OH}\\ \quad\quad|\\ \quad\text{OH}\end{array}$, respectively, were used in place of the monool PIB-OH.

The structure and number-average functionality ($\bar{F}_n$) of PIB-CA were determined by ^{1}H-NMR and FTIR spectroscopies. Figure 1(a) shows the ^{1}H-NMR spectrum of α-phenyl-ω-hydroxy polyisobutylene (PIB-OH). The resonances in the δ = 7.1–7.4 ppm range are associated with the five phenyl protons, and the resonance in the δ = 3.2–3.5 ppm region are due to the two terminal methylene protons. The ratio of the integrated area characteristic of phenyl protons to the area of the terminal methylene groups is a quantitative measure of these functional groups. The peaks in the δ = 0.7–1.9 ppm range are due to CH_3- and $-CH_2-$ protons and the peak at δ = 5.31 ppm is due to CH_2Cl_2 impurity in CD_2Cl_2. Figures 1(b) and 1(c), respectively, show the spectra of the precursor and the PIB-CA. In Fig. 1(c) the peaks at 7.03 and 6.61 ppm are due to the two protons on the carbon atom of the double bond $\underline{CH_2}$=C(CN)COO—. Integration, relative to the five phenyl protons (internal standard), indicates quantitative functionalization. Integration and correlation of the aromatic protons with the terminal CH_2= C(CN)— protons were also used in the case of the linear di- and the tri-arm star telechelics to yield the number-average functionality ($\bar{F}_n$). Table 1 shows F_n of the various polymers obtained.

FTIR spectroscopy was used to substantiate the quantitative conver-

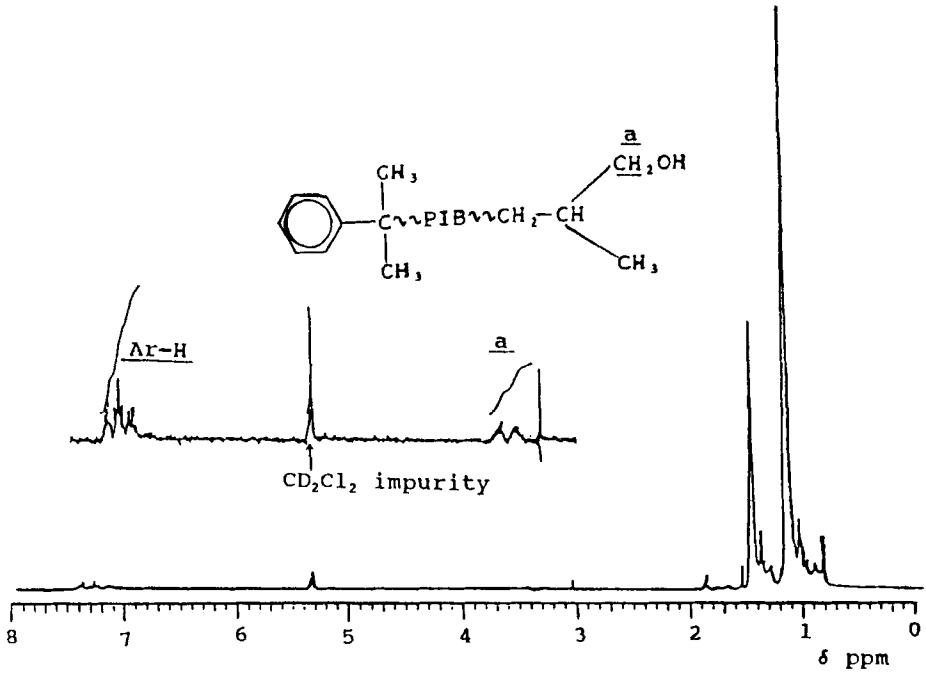


FIG. 1(a). ^{1}H-NMR spectrum of PIB-OH.

sion of $-CH_2OH$ to $-OCO-C(CN)=CH_2$ end-groups. A representative FTIR spectrum of PIB-OH is shown in Fig. 2(a). The strong broad absorption at 3300 cm^{-1} is due to the terminal hydroxyl group. In Fig. 2(b) the new peaks at 2247 and 1738 cm^{-1} are due to the $-CN$ and $-CO-$ groups, respectively, and the disappearance of the $-OH$ peak at 3300 cm^{-1} indicates the complete conversion of $-CH_2OH$ to $-OOC-C(CN)=CH_2$ end-groups.

B) Polymerization of Telechelic Macromers

While the cyanoacrylates are very reactive and rapidly polymerize even in the presence of weak bases (for example, water [6, 7]), the homopolymerization of cyanoacrylate-capped macromers are expected to be relatively slow due to the long PIB moiety [11–14]. We have investigated the bulk homopolymerizability of linear and three-arm star telechelics

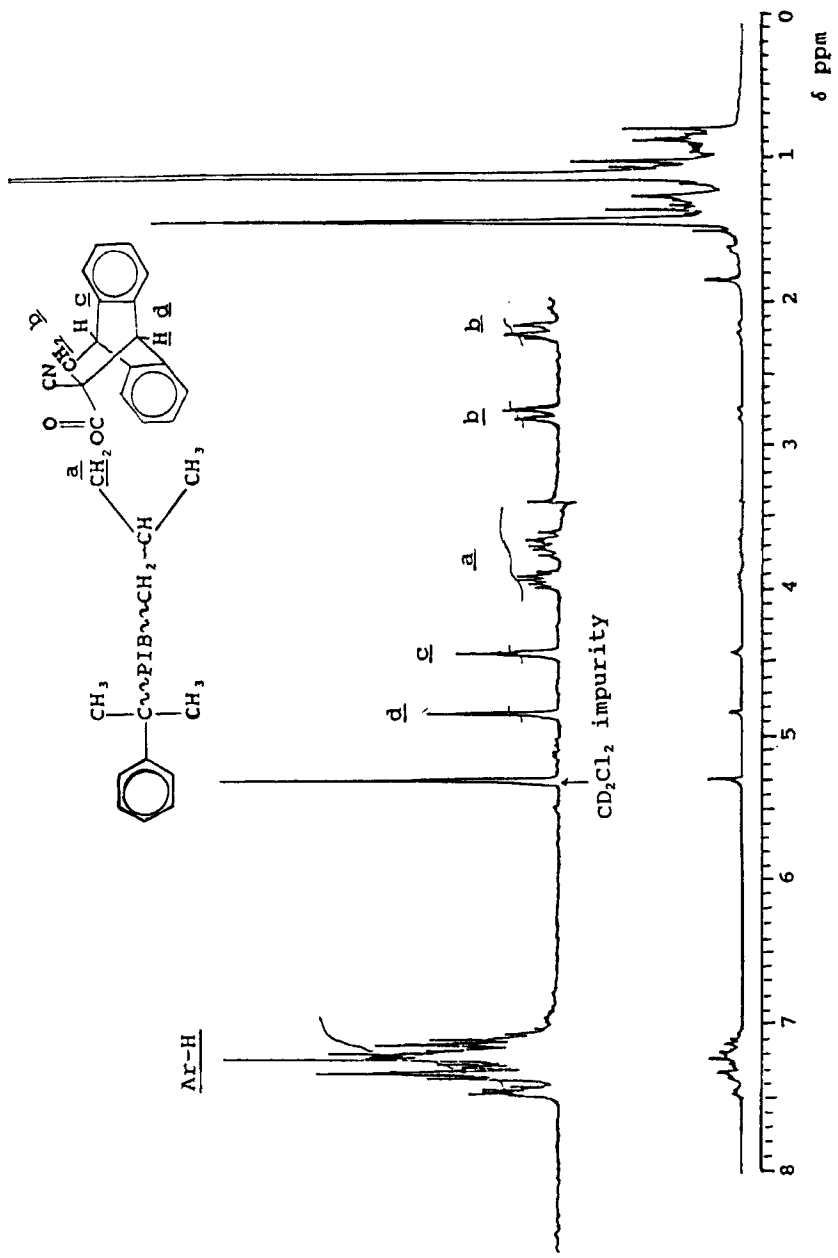


FIG. 1(b). ^{1}H-NMR spectrum of Product 3 in Scheme 2.

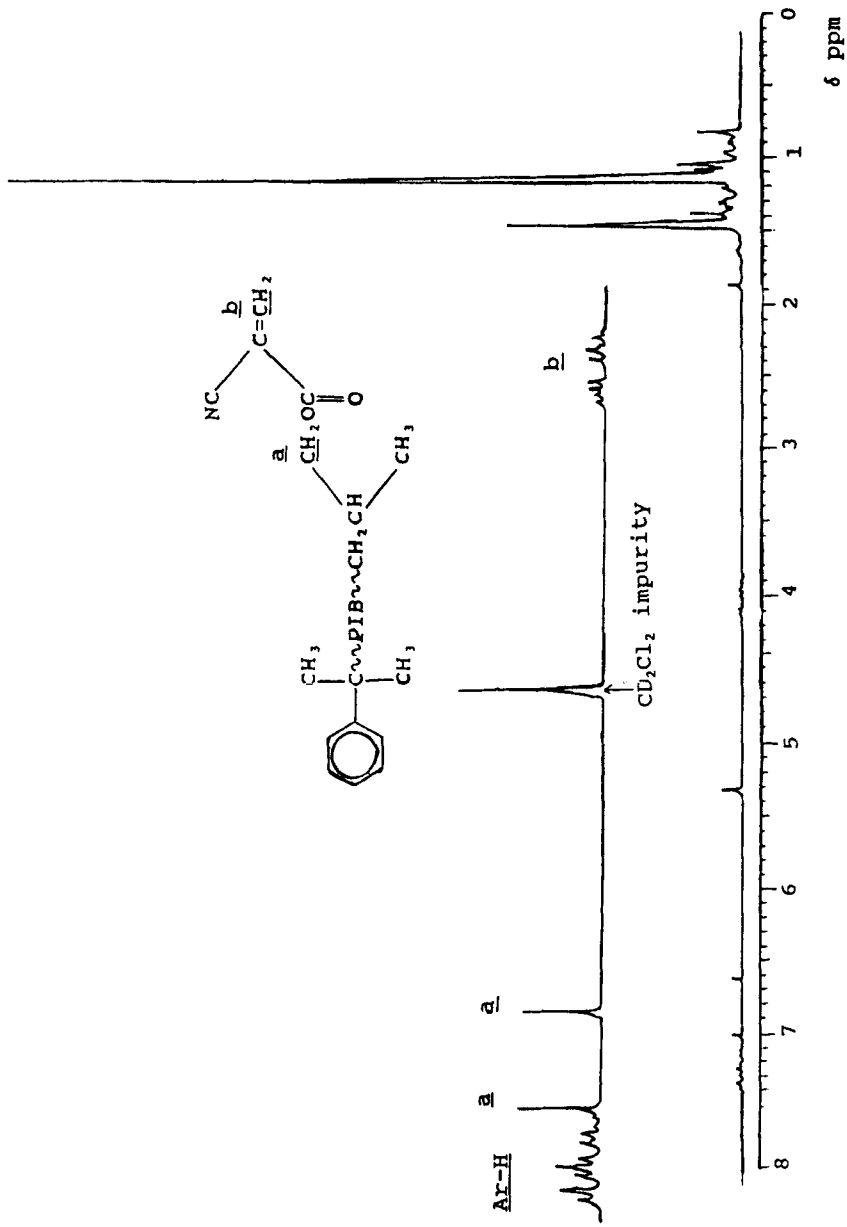


FIG. 1(c). ^{1}H-NMR spectrum of PIB-CA macromer.

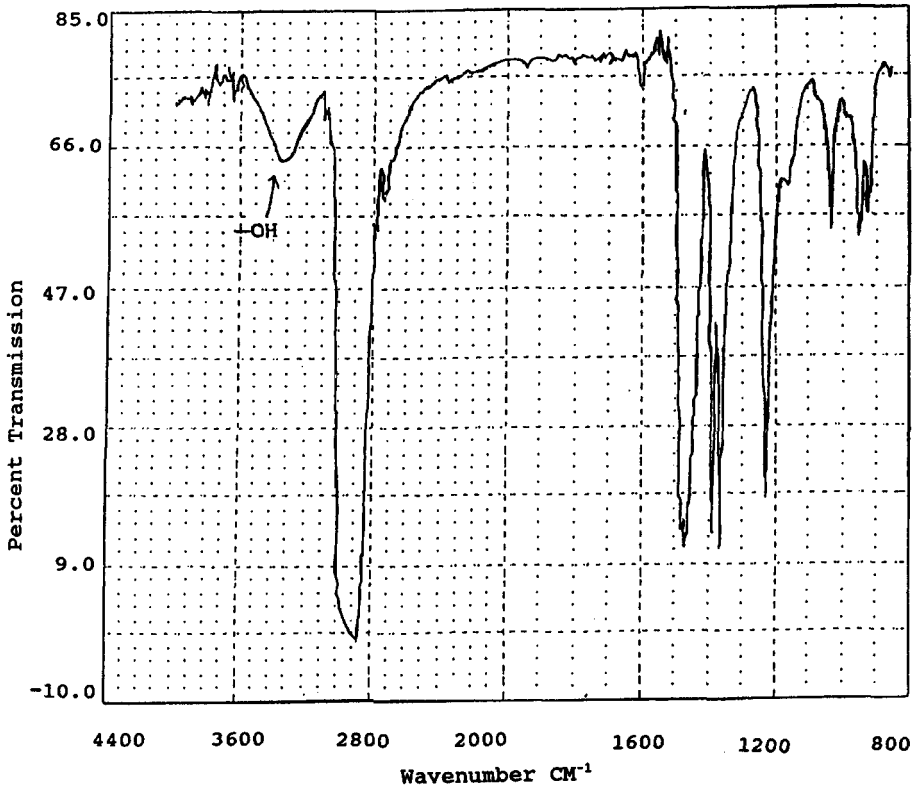


FIG. 2(a). FTIR spectrum of PIB-OH.

by exposing them to atmospheric moisture. The GPC trace (not shown) of the starting material and the product were compared; however, the traces indicated very little chain extension. The reason could be decreased chain-end(s) mobility due to the highly viscous system and/or the difficulty of contact between the hydrophobic PIB chains and OH^- (H_2O).

In another series of experiments the solution polymerizability of PIB-CA macromer was studied in the presence of anionic initiator DMT (see Experimental section). Figures 3(a) and 3(b) show the GPC traces of the PIB-CA ($\overline{M}_n$ = 2380; $\overline{M}_w/\overline{M}_n$ = 1.16) starting material and that of the product harvested. Evidently a high molecular weight product ($\overline{M}_n \approx$

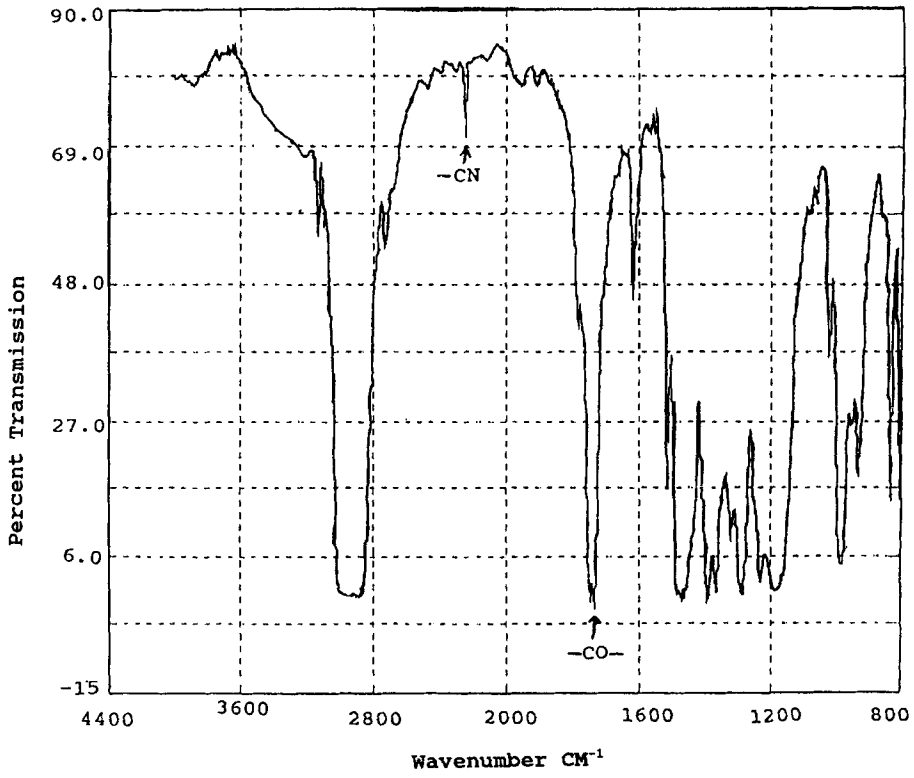
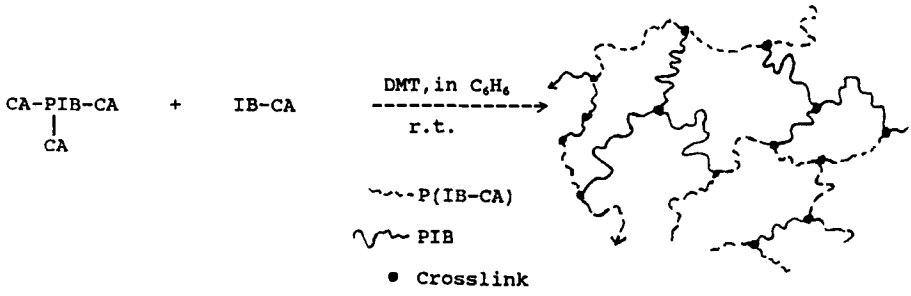


FIG. 2(b). FTIR spectrum of PIB-CA macromer.

35,000) was formed. According to the GPC trace, the high molecular weight fraction was ~73 wt% of the final product. Incomplete polymerization may be due to the increasing viscosity of the system and/or decreasing concentration of reactive end-groups.

We have investigated the crosslinkability (polymerizability) of di- and tri-arm star PIB telechelics by DMT. Table 1 gives experimental details and the percent of sol fractions obtained. The crosslinked telechelics are clear flexible films, and the low sol fractions indicate a high degree of crosslinking.

In another experiment a copolymerization of a tri-arm telechelic PIB with IB-CA was carried out to obtained the network. Schematically:



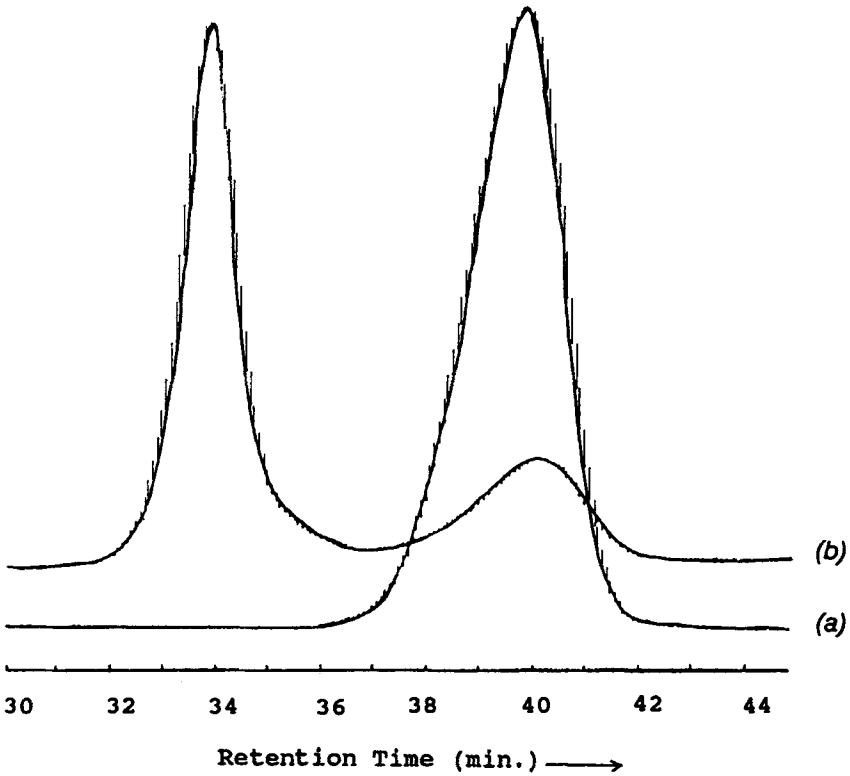


FIG. 3. GPC traces of (a) PIB-CA macromer (starting material) and (b) of the product harvested after solution polymerization. [Macromer] = 0.025 *M*, [DMT] = 0.005 *M*, benzene solvent, 8 h.

The network obtained was swelled both in hexanes (40 wt% after 2 days) and in nitromethane (90 wt% after 2 days), which indicates formation of a polar/nonpolar two component network.

The 2-cyanoalkyl acrylates have been found to polymerize in contact with proteinaceous substrates [15, 16]. We have investigated the polymerizability of our telechelic macromers in the presence of various proteinaceous materials. Of the various substances tried, human blood and egg yolk were found to cause chain extension. Thus di- and three-arm star telechelics were mixed with drops of human blood or egg yolk on a glass plate. After 1 day of contact the viscosity of the blend increased noticeably, indicating a measure of chain extension.

In summary, cyanoacrylate-capped PIBs were shown to homo- and copolymerize readily to high molecular weight products. These prepolymers are expected to yield interesting new coatings and adhesives or, in conjunction with conventional cyanoacrylates, water-resistant polycyanoacrylates.

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