

Isocyanate-Terminated Polybutadiene Prepolymers: Synthesis, Characterization, and End-Group Modifications

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Synopsis

Telechelic prepolymers of butadiene with aliphatic isocyanate end-groups were prepared by the solution polymerization of butadiene under free radical initiation. 4,4'-Azobis (4-cyanopentanoyl azide) was used as the initiator. Liquid prepolymers were obtained with molecular weights of 1450 to 6000 and functionalities 1.9 to 2.2. The prepolymers were characterized by their number-average molecular weight, isocyanate content, functionality, infrared, and nuclear magnetic resonance spectra and microstructure. The storage stability of the prepolymers was checked and they were found to be quite stable under ambient conditions. Isocyanate-terminated polybutadienes were reacted with *N,N*-dimethylamino ethanol and *t*-butyl hydroperoxide to obtain useful dimethylamino-terminated and peroxy-carbamate-terminated prepolymers, respectively.

INTRODUCTION

Polybutadienes possessing isocyanate end groups are interesting as prepolymers for the synthesis of polyurethanes having superior hydrolytic stability.^{1,2} Furthermore, due to the high reactivity of isocyanate group with alcohols and amines, isocyanate-terminated prepolymers can easily be modified, cross-linked, grafted, and so on.

Isocyanate-terminated polybutadienes are prepared, as a rule, by reacting preformed hydroxyl-terminated polybutadienes with an excess of a diisocyanate. Recently, we have reported³ the synthesis of a new free radical azo initiator, namely 4,4'-azobis (4-cyanopentanoyl azide) [ABAZ] and its convenience and effectiveness in the synthesis of isocyanate-terminated polyisoprenes was demonstrated.

The present paper reports the synthesis of aliphatic isocyanate-terminated polybutadienes by using ABAZ as the initiator. Polybutadienes of different molecular weight were obtained by varying initiator concentration. Polybutadienes were characterized by the number average molecular weight (\bar{M}_n), isocyanate content, functionality, infrared (IR) and nuclear magnetic resonance (NMR) spectra, and microstructure. Isocyanate-terminated polybutadienes were further reacted with *N,N*-dimethylamino ethanol and *t*-butyl hydroperoxide to obtain useful dimethylamino-terminated and peroxy-carbamate-terminated prepolymers, respectively.

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EXPERIMENTAL

Materials

1,3-Butadiene, supplied by M/s NOCIL, Bombay was purified by passing through a series of three scrubbers, each containing ethylene glycol/ethylene glycolate to remove moisture in the monomer. Anhydrous ethylene glycol (150 mL) in which sodium (2 g) had been dissolved was added to each gas scrubber. The system was purged with argon to remove air before use. Butadiene was passed through the scrubbers, then through a Drierite column, and finally condensed in a graduated vessel immersed in a dry ice-acetone bath. About 100 mL of the monomer was collected over a period of 1 h.

1,4-Dioxane was carefully purified as described by Vogel.⁴ Finally, it was dried over CaH_2 and then distilled. 4,4'-Azobis (4-cyanopentanoyl azide) was prepared as described previously³ and used immediately after its preparation.

Polymerization Procedure

Required quantities of initiator and solvent were taken into a thick-walled glass ampoule and degassed at 10^{-2} mmHg by three freeze-pump-thaw cycles. Required quantity of butadiene was taken in another ampoule and degassed in a similar manner and butadiene was then distilled into the ampoule containing the initiator and solvent. After complete distillation of butadiene, the ampoule was carefully sealed under vacuum. After separation from the manifold, the ampoule was sheathed in a glass cloth and placed in a thermostat controlled to $\pm 0.1^\circ\text{C}$ for 72 h. The reaction was stopped by freezing in liquid nitrogen. The ampoule was opened, unreacted butadiene was allowed to boil off, and the contents of the ampoule were transferred into a round-bottom flask. Dioxane was removed on a rotary evaporator. Finally, the low molecular weight materials were removed by heating the prepolymer samples at 80°C under vacuum (10^{-5} mmHg) for several hours.

Analytical Procedures

Number-average molecular weight (\bar{M}_n) determinations were made on a Knauer vapor pressure osmometer (VPO) with toluene as solvent at 45°C . The isocyanate content was determined using standard analytical technique.⁵ The dimethylamino content of the polymer was determined by an acid-base back titration method.⁶ The polymer was analyzed for peroxygen content by iodine-thiosulfate titration.⁷ The microstructure was determined by IR spectroscopy using 2.5% solution of sample in CS_2 .⁸ The spectra were recorded on a Perkin-Elmer model 221 spectrophotometer. NMR spectra at 60 MHz of prepolymers in CCl_4 were recorded at room temperature using TMS as an internal standard on Perkin-Elmer R-32 instrument.

RESULTS AND DISCUSSION

4,4'-Azobis(4-cyanopentanoyl azide)-initiated homopolymerization reactions of butadiene were carried out on a 0.2 mole scale employing a conventional free radical polymerization technique. A carefully purified anhydrous dioxane was used as the solvent. Table I summarizes the results of polymerization of

TABLE I
 Synthesis of Isocyanate-Terminated Polybutadiene Prepolymers^a

Expt. no.	Initiator concentration mol% (based on butadiene)	Yield (%)	Number average molecular weight (\bar{M}_n)	Equivalent weight (NCO)	NCO content (%)	Functionality (NCO)
1	0.5	30	6000	2730	1.54	2.2
2	1	39	3050	1400	3.0	2.2
3	2	52	2220	1170	3.59	1.9
4	3	59	1980	990	4.24	2.0
5	5	69	1450	660	6.36	2.2

^a Conditions of polymerization: Butadiene concentration = 6 mol/L; polymerization time = 72 h; polymerization temperature = 65°C; solvent = dioxane.

butadiene. Initiator concentration was varied from 0.5 to 5 mol%. Polybutadiene yields increased with increase in initiator concentration. Molecular weight (\bar{M}_n) of the prepolymers decreased with an increase in initiator concentration, as expected from free radical polymerization reactions.

Functionality values of the prepolymers were obtained from the expression, functionality (f) = \bar{M}_n (by VPO)/equivalent weight, where equivalent weight was obtained from isocyanate group content. Functionality values of the prepolymers were found to vary in the range 1.9–2.2. Thus, these prepolymers have sufficient functionality for use in chain-extension reactions.

The IR spectrum, as shown in Figure 1, of a typical prepolymer showed all the bands characteristic of the polybutadiene chain.⁹ In addition, there was present a strong absorption band at 2260 cm^{-1} , which is characteristic asymmetric stretching vibration of the isocyanate group, thus, indicating the attachment of these groups to the polymer chain.

A representative NMR spectrum of isocyanate-terminated polybutadiene prepolymer is shown in Figure 2. In addition to the resonances due to the protons from the polybutadiene chain,^{10,11} a triplet was observed at 3.50 δ , which can be assigned to the methylene protons adjacent to the isocyanate group.

Microstructure determination of some selected samples by IR spectroscopy gave an approximate composition of 17% *cis*-1,4; 62% *trans*-1,4, and 21% vinyl, i.e., 1,2-contents. The results agree with the structure determined from NMR spectra using a known method¹² ($21 \pm 1\%$ vinyl and $79 \pm 1\%$ of total, 1,4-units). Thus, microstructure values were in the range commonly found in free radically prepared polybutadienes.¹³

The prepolymers, although containing reactive isocyanate groups, were found to be quite stable under ambient conditions. Extreme care was taken to avoid exposure of the prepolymers to moisture while preparing and isolating them. This included thorough drying of monomer, solvent, and apparatus used in the polymerization reactions. The storage stability was maintained by blanketing the samples with dry nitrogen gas before being sealed in a container. The isocyanate content of a typical prepolymer determined at intervals of 4, 8, 15, 21, and 30 days was found to be unchanged. The stability of prepolymers was also checked by comparing IR spectra of three-month-old

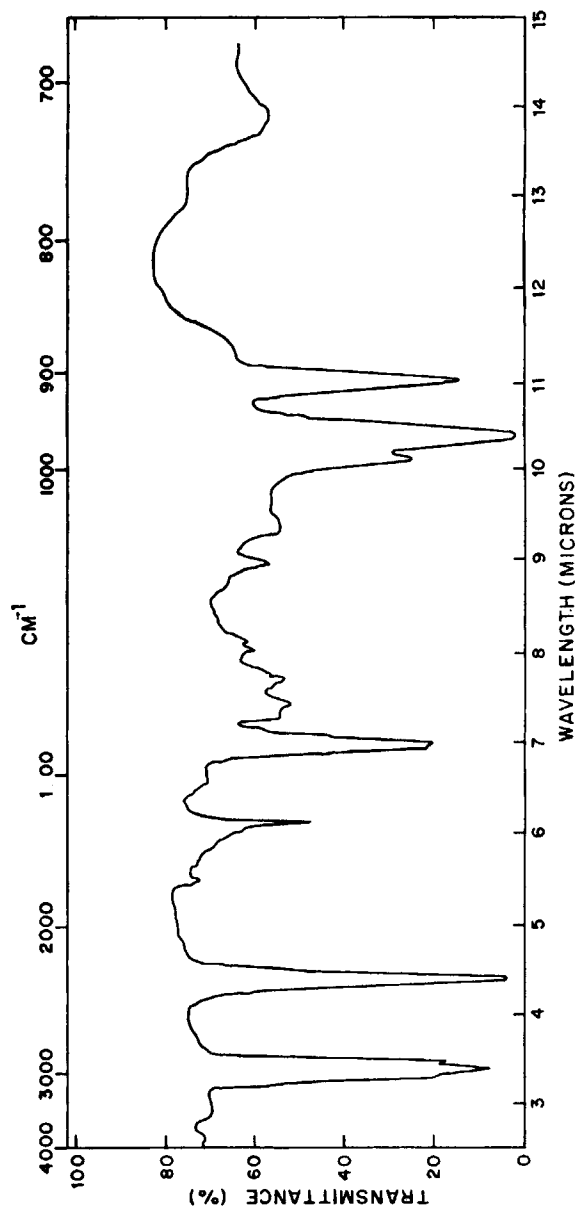


Fig. 1. IR spectrum (film) of isocyanate-terminated polybutadiene.

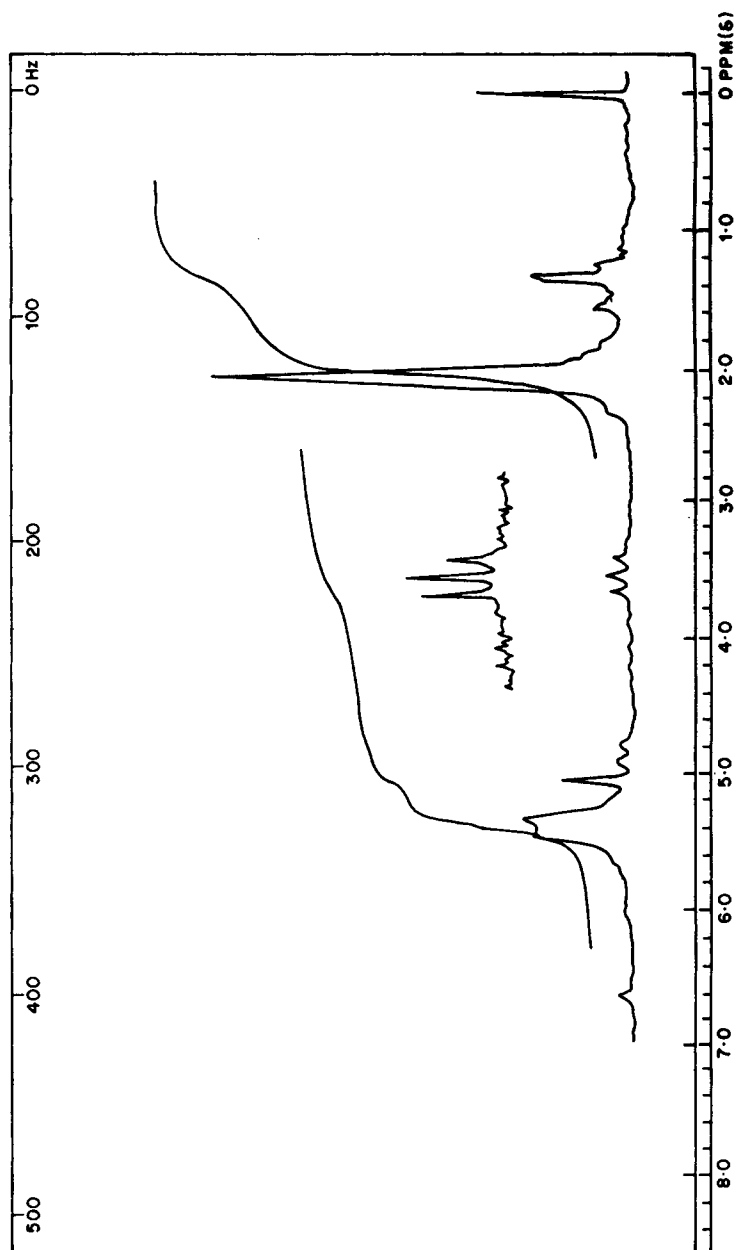


Fig. 2. NMR spectrum (in CCl_4) of isocyanate-terminated polybutadiene.

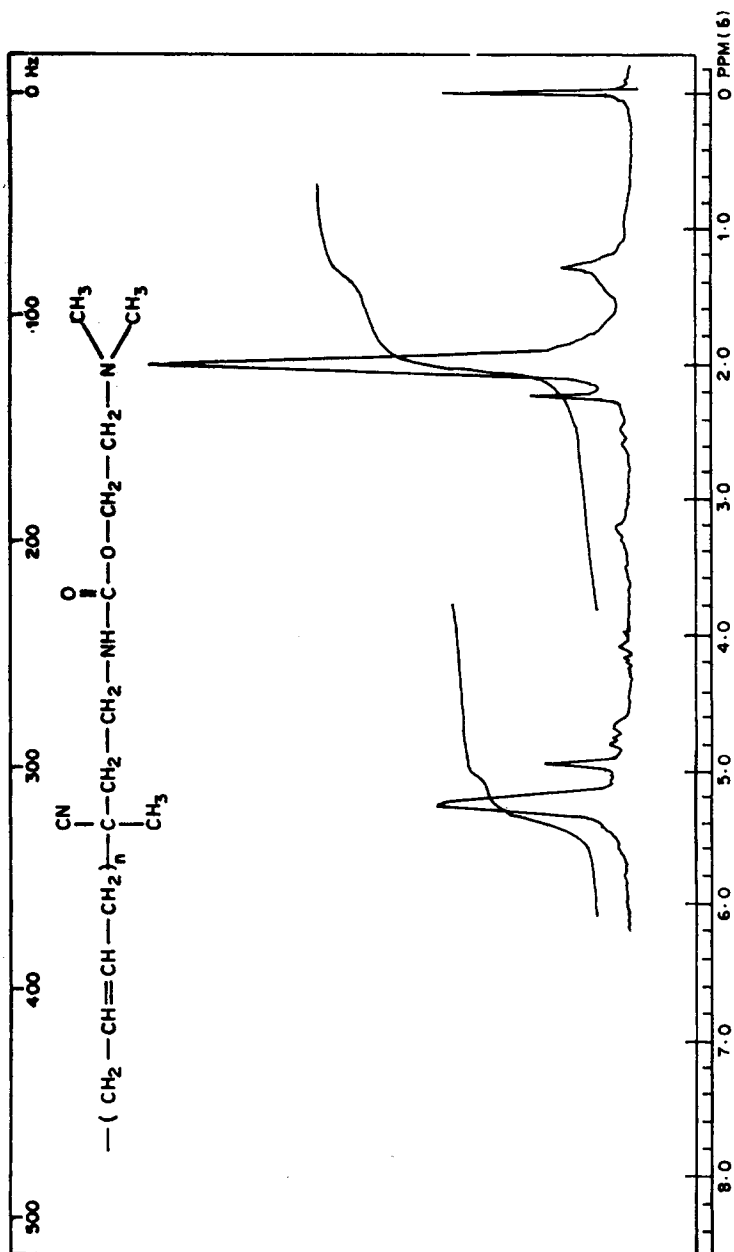


Fig. 4. NMR spectrum (in CCl_4) of tertiary amine-terminated polybutadiene.

samples with freshly prepared samples. The spectra were identical, indicating that the samples were stable over this time span.

The well known reactions of isocyanate group with active H-compounds suggested the possibility of using these isocyanate-terminated polydienes for the preparation of polymers possessing other interesting functional groups by end-group modifications. It is important in carrying out reactions on polymers that the reaction proceeds quantitatively because of the inherent difficulties in separating reacted from unreacted polymer. The isocyanate-hydroxyl reaction is ideal in the sense that it is known to give quantitative yields without formation of byproducts. Thus, isocyanate-terminated polybutadiene prepolymers were reacted with *N,N*-dimethylamino ethanol and *t*-butyl hydroperoxide to get dimethylamino-terminated and peroxy-carbamate-terminated prepolymers, respectively, as shown in Figure 3.

The reaction of isocyanate-terminated polybutadiene ($\bar{M}_n = 3050$, $f = 2.2$) with twofold excess of *N,N*-dimethylamino ethanol was carried out in benzene at reflux temperature. The course of the reaction was followed by IR spectrum. The IR spectrum of a sample after 2 h showed complete disappearance of the isocyanate group absorption at 2260 cm^{-1} . Benzene and excess *N,N*-dimethylamino ethanol were removed on a rotary evaporator and the polymer was purified by precipitation with methanol from benzene solution. The yield of the polymer was 95%. The IR spectrum of dimethylamino-terminated prepolymer showed the bands characteristic of urethane linkage:

3300 cm^{-1} (N-H stretching), and 1700 cm^{-1} ($\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$ stretching). It was difficult to identify the tertiary-amine end groups in the IR spectrum. However, the presence of *N,N*-dimethylamino end groups in the prepolymer was confirmed with the NMR spectrum (Fig. 4), which showed a sharp singlet at $2.30\ \delta$ due to the *N*-methyl protons. From the value of dimethylamino group content and molecular weight of the prepolymer ($\bar{M}_n = 3200$, as determined by VPO measurements), the functionality of prepolymer was found to be 2.2. This value was in excellent agreement with the NCO-functionality of the starting prepolymer. The tertiary amine-terminated polybutadienes represent valuable intermediates in the synthesis of ionene polymers.¹⁴

Polybutadiene possessing aliphatic isocyanate end groups ($\bar{M}_n = 3200$, $f = 2.2$) was reacted with twofold excess of *t*-butyl hydroperoxide in benzene at room temperature in the presence of a drop of dibutyl tin dilaurate as a catalyst. The IR spectrum indicated that the reaction was complete within half an hour. The product polymer was purified by precipitation with methanol. The prepolymer was finally dried under vacuum (10^{-5} mmHg) at 30°C for several hours. The yield of the polymer was 95%. From the value of peroxygen content and molecular weight of the prepolymer ($\bar{M}_n = 3200$, as determined by VPO), the functionality of prepolymer was found to be 2.1, indicating that the conversion of isocyanate groups to peroxy-carbamate groups was almost complete. Polybutadienes with peroxy-carbamate end groups can be used to initiate the polymerization of vinyl monomers to prepare block copolymers.¹⁵

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