

Crosslinking of Isocyanate Functional Acrylic Latex with Telechelic Polybutadiene. I. Synthesis and Characterization

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ABSTRACT: An ambient curable isocyanate functional acrylic latex was synthesized by incorporating dimethyl meta-isopropenyl benzyl isocyanate (TMI[®]), an isocyanate monomer, into styrene/*n*-butyl acrylate copolymer. An artificial latex of amino-terminated telechelic polybutadiene was prepared and blended with the acrylic latex as a curing agent. The isocyanate content in the blended latex was determined by titration and FTIR measurements. The latex blend properties, in terms of particle size and latex viscosity, and the latex film properties, in terms of stress-strain behavior and solvent swelling behavior, showed no significant change after 30 days' storage of the latex blend at 50°C. The good storage stability was attributed to the stable nature of the latex blend in which there was little chance for the isocyanate-containing particles to come into contact with the curing agent particles, thus preventing premature contact of the acrylic chains with the telechelic chains. The reactivity of different functional groups in the telechelic polymer was studied; the amino group was found to be the most reactive toward the TMI. In addition, a shorter chain telechelic crosslinker was found to result in a higher degree of crosslinking, but this was more intraparticle than interparticle in nature. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 965–975, 1998

Key words: isocyanate functional latex; telechelic polybutadiene; amino terminated polybutadiene; latex blend; latex film crosslinking

INTRODUCTION

Thermosetting acrylic latices containing carboxyl or hydroxyl functional groups are commonly seen.^{1–3} Isocyanate functional acrylic latices have not received much attention, mainly because isocyanates hydrolyze in aqueous media, resulting in prematurely crosslinked particles. Dimethyl meta-isopropenyl benzyl isocyanate (TMI[®], Cytec Industries) is a relatively stable isocyanate monomer possibly because its isocyanate group is protected against water attack by the two neighboring methyl groups. TMI can be copolymerized with acrylic monomers by conventional emulsion

polymerization without significant loss of the isocyanate in the copolymer backbone.^{4–7} However, fully cured networks can be achieved only at elevated temperatures without adding any catalyst when the TMI content is within the normal range (~2 wt % based on monomer). Room temperature curing requires ~ 10% TMI. This high TMI content not only increases the cost, but also results in short shelf-life. One solution to this problem is to use an external curing agent. Curing agents for isocyanates or polyurethanes are usually polyols and polyamines, which should be packed separately from the isocyanate when the latter is not blocked. In this article a model system comprising a latex blend is presented in which an isocyanate-containing styrene/*n*-butyl acrylate/TMI copolymer latex is in one component, and the curing agent, an amino-terminated telechelic polybuta-

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diene (PBD) latex, is the other component. Telechelic polymers are low-molecular-weight polymers having reactive chain ends. The synthesis and characterization of the amino-terminated telechelic PBD was reported previously.⁸ Here, the telechelic PBD was chosen as the curing agent instead of a low-molecular-weight polyamine, partly because it is conveniently made into an artificial latex.⁹ In theory, when the isocyanate and the curing agent are separated into two types of particles in the blend, curing should not occur during storage as long as the latex blend is stable (without coagulation) since the isocyanate and the curing agent have little chance to come into contact with each other. Ambient curing can be achieved upon application of the latex blend as a film; when the water evaporates, the two types of particles contact each other (coalescence) and the telechelic PBD chains diffuse into the acrylic particles.

EXPERIMENTAL

Materials

Styrene (St, Aldrich, Milwaukee, WI) and *n*-butyl acrylate (BA, Aldrich) monomers were passed through inhibitor removal columns (Aldrich Cat. #30, 631-2 for BA and Cat. #30, 632-0 for St) before use. Dimethyl meta-isopropenyl benzyl isocyanate (TMI®, Cytec Industries) was used as received. Sodium lauryl sulfate (SLS, Aldrich), aerosol MA (sodium dihexyl sulfosuccinate, Cytec Industries), potassium persulfate ($K_2S_2O_8$, Aldrich), and potassium metabisulfite ($K_2S_2O_5$, Aldrich) were used as received. Water was distilled and deionized (DDI).

Batch Polymerization of the St/BA/TMI

Styrene (8.00 g), 8.00 g of *n*-butyl acrylate, 0.3266 g of the TMI, 0.300 g of the SLS, and 35 g of water were placed in a 250 mL three-neck flask fitted with a stirrer and a condenser under a nitrogen (Zero grade, JWS Technologies) atmosphere at 40°C. Potassium persulfate (0.05 g) and 0.05 g potassium metabisulfite were added as stock solutions ($K_2S_2O_8$ /water = 0.04 g/mL, $K_2S_2O_5$ /water = 0.04 g/mL). The conversion of the polymerization was monitored via gas chromatography (GC). Polymerization was completed within five hours. The particle size of the poly(styrene/*n*-butyl acrylate/TMI) (PSBT) latex as determined by

capillary hydrodynamic fractionation (CHDF) was 80 nm.

Semicontinuous Polymerization of the St/BA/TMI

Styrene (4.00 g), 4.00 g *n*-butyl acrylate, 0.1633 g TMI, 0.600 g of aerosol MA 80, and 73 g water were placed in a 250 mL three-neck flask fitted with a stirrer and a condenser under a nitrogen atmosphere at 40°C. Potassium persulfate (0.10 g) and 0.10 g potassium metabisulfite were added from stock solutions as above. The polymerization was carried out for 30 min to form seed particles prior to beginning the feed. Then, the monomers (4.50 g styrene, 4.50 g *n*-butyl acrylate, 0.1837 g TMI), the oxidant ($K_2S_2O_8$ /water = 0.1366 g/9.5 mL), and the reductant ($K_2S_2O_5$ /water = 0.1366 g/9.5 mL) were fed in three separate syringes at a rate of 0.08 mL/min using a syringe pump (Harvard Apparatus, Model 22). After the completion of the feeding, the polymerization system was maintained under agitation for four more hours so that no unreacted monomers were left in the flask (checked by GC). Latex (63.5 g) (labeled latex A) was removed from the flask. To the remainder of the latex was fed the second part of the monomers (5.00 g styrene, 5.00 g *n*-butyl acrylate, 0.2041 g TMI), the oxidant ($K_2S_2O_8$ /water = 0.1625 g/11.3 mL), and the reductant ($K_2S_2O_5$ /water = 0.1625 g/11.3 mL), in the same manner as for the first feeding. Four hours after the completion of the feeding, 54 g latex (labeled latex B) was removed from the flask. Finally, the third part of the monomers (5.30 g styrene, 5.30 g *n*-butyl acrylate, 0.2165 g TMI), the oxidant ($K_2S_2O_8$ /water = 0.1726 g/12 mL), and the reductant ($K_2S_2O_5$ /water = 0.1726 g/12 mL) were fed into the flask. The final latex was labeled latex C.

Gas Chromatography (GC)

A Hewlett Packard 5890 GC with an HP 3393A computing integrator was used. The injection port temperature was 200°C. The oven temperature was set at 70°C for 3 min before being raised to 170°C at a rate of 20°C/min for 5 min. Helium, hydrogen, and air flow rates were 30 mL/min, 32 mL/min, and 400 mL/min, respectively.

Titration of the Isocyanates in the PSBT Polymers

A portion of each latex was first freeze-dried and then ~ 2 g of the freeze-dried polymer was weighed to 0.0001 g and dissolved in 80 mL tolu-

Table I Characteristics of the Amino-Terminated Telechelic PBD Artificial Latex

% Solids	PBD (mol)/latex (g)	Surfactant	Particle Size (nm, CHDF)					$f_{\text{NH}_2}^{\text{a}}$	M_n^{b}
			D_n	D_w	PDI	D_v			
4.74	1.09×10^{-5}	SLS	47	52	1.11	50	2.0	3100	

^a f_{NH_2} , amino functionality.

^b M_n , number average molar weight (g/mol) determined by gel permeation chromatography.

ene in a 250 mL Erlenmeyer flask before 7.0 mL of 0.05N dibutyl amine solution in toluene was added. 2-Propanol (80 mL) was added to this solution, which was then titrated with 0.0200N HCl standard solution (Fisher SA-601). The endpoint was determined with bromphenol blue indicator (0.1% solution, prepared by mixing 0.10 g acid, non-water-soluble bromphenol blue with 1.5 mL 0.1N sodium hydroxide solution and diluting to 100 mL with water).

FTIR Analysis

A Mattson Sirius FTIR spectrophotometer (Model 100) was used for the FTIR analysis. A polymer latex sample was cast onto a zinc-selenide disk (Janos Technology) at room temperature and air-dried to obtain a thin film before the FTIR analysis. Each sample was analyzed four times by rotating the disk 90° for each measurement and the results were averaged.

PBD-NH₂ Artificial Latex

Amino-terminated telechelic polybutadiene (designated PBD-NH₂)⁸ was dissolved in toluene (7.3 g in 30 g toluene) before mixing with a solution of SLS in water (2 g in 90 g water). After ultrasonification (60 s, power 6; 50% duty cycle; model W350, Branson Sonic Power Co.) and stripping of the toluene and part of the water, a PBD-NH₂ artificial latex was obtained. The characteristics of this PBD-NH₂ latex are listed in Table I.

Capillary Hydrodynamic Fractionation (CHDF)

A Matec high-resolution CHDF-1100 instrument (Matec Applied Science) with Matec GR-500 eluant solution was employed to obtain particle size distributions and averages. Volume average particle diameters are reported in this article.

Latex Viscosity

A Brookfield Synchro-Lectric viscometer model LVT with an 18/13R spindle was used; the viscosity of the latex samples was measured at different shear rates.

Latex Film Formation

Latex films for film property studies were formed by casting the latex onto a glass plate at room temperature and drying for more than 7 days. The amount of the latex used and the area of the plate were determined by the solids content of the latex in order to obtain a dry film thickness 0.3 to 0.6 mm.

Latex Film Stress–Strain Behavior

An Instron universal tensile testing machine (model 1011) was used for measuring stress–strain behavior of the PSBT/PBD-NH₂ latex films. Standard microtensile test specimens were used according to the ASTM D1708-84 method. A 500 Newton load cell was employed, and the experiments were carried out at a crosshead speed of 25 mm/min.

Solvent Swelling Ratio

A circular piece of the PSBT/PBD-NH₂ latex films having a 14-mm diameter was placed in toluene for 48 h. The swelling ratio of the film was taken as w/w_0 , where w_0 and w were the weights of the film before and after being swollen in toluene, respectively.

¹³C-NMR Study

A Bruker AM-500 was employed for measurement of the NMR spectra (SF: spectrometer frequency = 125.8 MHz; SW: spectral width = 29412 Hz; TD: time domain data = 65536; LB: line broadening

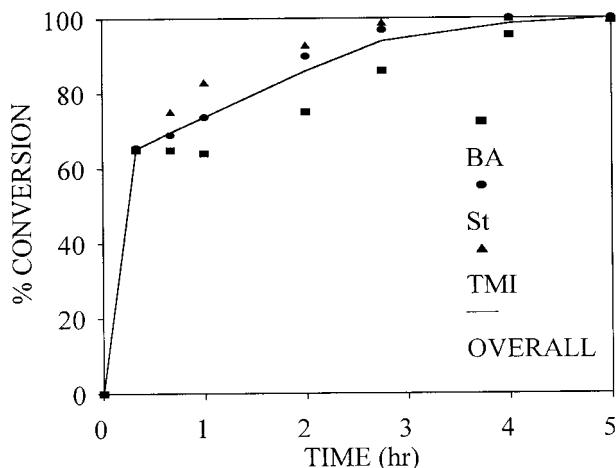


Figure 1 Conversion versus time curves for the three monomers in the batch emulsion copolymerization of St/BA/TMI; $T_r = 40^\circ\text{C}$.

= 1 Hz; NS: number of scans = 500 to 2000). In all cases, deuterated chloroform ($\delta = 77$ ppm) was used as solvent.

TMI Reaction with the PBD-NH₂

TMI (0.200 g) was added to 1.000 g PBD-NH₂ ($M_n = 2400$) in 100 mL THF under nitrogen. The mixture was stirred for one hour before about half of the THF was evaporated. Ethanol (50 mL) was added to the system to precipitate the product. The precipitate was washed with ethanol three times to remove the unreacted TMI before being vacuum-dried for 24 hours. A colorless viscous product, designated PBD-TMI, was obtained.

RESULTS AND DISCUSSION

PSBT Latex

The isocyanate functional acrylic latex, poly(St/BA/TMI), was prepared by conventional emulsion polymerization. The individual and overall conversion-time behaviors for the batch process are shown in Figure 1. Note that the TMI monomer was consumed faster than the BA and the St. Since TMI is more hydrophobic than BA, the isocyanate groups of the TMI units might be expected to be distributed randomly inside the particles instead of on the particle surfaces.

Determination of the Isocyanate Content in the PSBT Latex

Although the isocyanate group in the TMI is relatively stable compared with other isocyanates, it still hydrolyzes to a certain degree. Therefore, the final isocyanate content in the latex may differ from that in the original recipe. In this experiment, nine PSBT latex samples were synthesized with varying amounts of TMI. The latices were freeze-dried in order to remove the water without hydrolysis of the isocyanate groups, so that the isocyanate content in the dry polymer was the same as in the latex. The percent TMI in the dry polymer was determined by titration as follows. An excess amount of dibutyl amine was used to completely react the NCO in the sample, and then the remaining dibutyl amine was back-titrated with an HCl standard solution. The results are listed in Table II. Comparing the percent TMI

Table II Determination of Percent TMI in the PSBT Latex Polymers

Sample	% TMI in Monomers	Polymer (g) for Titration	V_{HCl} (mL)	% TMI in Polymer ^a	Lost TMI ^b (%)
A	0	2.042	16.85	N/A	N/A
B	0.26	2.042	15.54	0.26	0
C	0.53	2.066	14.25	0.52	2.4
D	0.89	2.048	12.84	0.81	8.5
E	1.20	2.061	11.19	1.14	5.0
F	1.74	2.109	8.66	1.61	7.6
G	1.91	2.074	7.42	1.88	1.4
H	2.61	2.182	4.20	2.40	7.9
I	3.48	2.088	0.09	3.32	4.5

^a % TMI in polymer = $(V_A - V) \times 0.02 \times 201.3 \times 10^{-3} \times 100 / W_{\text{Polymer}}$, where V_A is the volume of HCl (mL) for sample A (blank); V is the volume of HCl (mL) for the specific sample; 0.02 is the molar concentration of the HCl solution; 201.3 is the molecular weight of TMI; and W_{Polymer} is the weight of the polymer sample used in the titration (g).

^b (% TMI added - % TMI in polymer) \times 100/% TMI added.

Table III Titration of the TMI Solutions in Toluene

	1	2	3	4	5	6	7
TMI added	0	0.0294	0.0760	0.1215	0.1752	0.2429	0.2931
V_{HCl} (mL)	75.90	68.65	56.72	44.90	31.20	16.95	4.38
TMI titrated (g) ^a	0.0000	0.0292	0.0772	0.1248	0.1800	0.2373	0.2879
% Deviation	0.0	-0.6	1.6	2.7	2.7	-2.3	-1.8

^a TMI (g) = $(V_1 - V) \times 0.02 \times 201.3 \times 10^{-3}$, where V_1 is the volume of HCl (mL) for sample 1 (blank); V is the volume of HCl (mL) for the specific sample; 0.02 is the molar concentration of the HCl solution; and 201.3 is the molecular weight of TMI.

added in the recipe (based on monomer) and the percent TMI in the polymers found by titration, the lost TMI was from 2 to 8%. This is inconsistent with previous results obtained via GC in our lab⁷ that showed that nearly all of the TMI was copolymerized in an emulsion polymerization of methyl methacrylate and BA with TMI. The loss of TMI in the present study is most likely due to the hydrolysis of the NCO groups during the polymerization process.

The validity of the titration method was checked by titrating a series of TMI solutions of different concentration in toluene. It can be seen from Table III that the standard deviations of the titrated results were within $\pm 3\%$.

The hydrolysis of the NCO groups would lead to the formation of urea linkages between polymer chains, which is the basic crosslinking mechanism of polyurethanes. However, all the PSBT samples for the titration analysis were fully soluble in toluene because the degree of the hydrolysis was low.

In cases where titration analysis of the isocyanate groups are inconvenient or even impossible, FTIR analysis may provide an alternative. The NCO absorption at 2258 cm^{-1} can be used for quantitative analysis in conjunction with the phenyl (Ph) absorption of the styrene units in the PSBT at 1605 cm^{-1} as the internal standard. An

FTIR spectrum of the PSBT sample is shown in Figure 2(a). A baseline method^{10,11} was used to determine the absorbance values in the FTIR spectra. A calibration curve for the FTIR analysis was established by plotting the NCO/Ph absorbance ratio of the nine PSBT samples in Table II against the corresponding percent TMI data from the titrations, as shown in Figure 2(b).

Particle Size and pH Effects

As described in detail earlier, three PSBT latices having different particle size were prepared by semicontinuous emulsion polymerization in which the monomers were fed to the polymerization system in three stages, A, B, and C. Before the start of stage B, a portion of the latex was removed from the system and labeled latex A. Latices B and C were obtained similarly. The particle sizes of the three latices as determined by CHDF, and the TMI concentration in the latex films as determined by FTIR, are listed in Table IV.

In the FTIR analysis, the latices were cast onto FTIR disks and dried for 24 h. During the drying process, 10 to 25% of the TMI in the latex particles underwent hydrolysis. It can be seen that the degree of hydrolysis increased with decreasing particle size. The increasing specific particle sur-

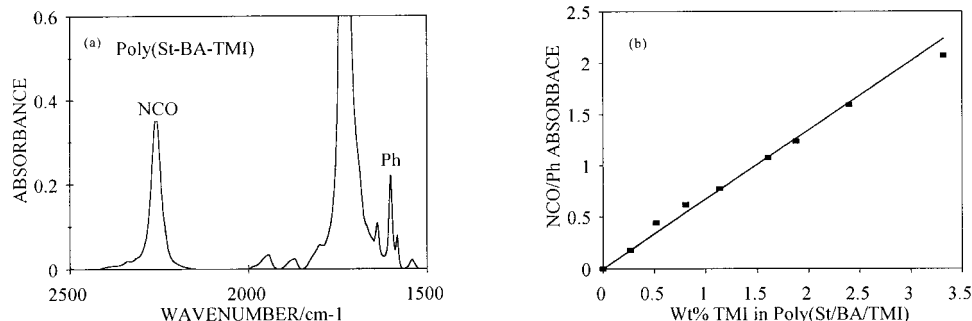


Figure 2 (a) FTIR spectrum of a PSBT sample; (b) FTIR calibration curve of the %TMI in the PSBT samples; NCO/Ph absorbance = NCO at 2258 cm^{-1} /Ph at 1605 cm^{-1} .

Table IV Effect of Particle Size on TMI Hydrolysis

	Latex A	Latex B	Latex C
% St in latex ^a	49.0	49.0	49.0
% BA in latex ^a	49.0	49.0	49.0
% TMI in latex ^a	2.0	2.0	2.0
% TMI in film	1.5	1.7	1.8
% Hydrolyzed TMI	25	15	10
D_v (nm)	175	232	303

^a Based on monomers in the original recipe.

face area (cm^2/g) with decreasing particle size increased the contact of the TMI groups with water, thus leading to the increased amounts of hydrolysis.

In another experiment, the effect of latex pH on its TMI content was monitored as a function of time. Immediately following the polymerization, the PSBT latex was acidic; this was due to the SO_2 or H_2SO_3 generated by the redox initiator ($\text{S}_2\text{O}_5^{2-} + \text{S}_2\text{O}_8^{2-} \rightarrow \cdot\text{OSO}_2^- + \text{OSO}_3^- + \text{SO}_4^{2-} + \text{SO}_2$; $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$). Suppose the initiator concentration was 0.08 g/50 g H_2O ($7.2 \times 10^{-3} M$), the pH of the latex could then be estimated as:

$$[\text{H}^+] = \sqrt{K_a C} = \sqrt{(1.3 \times 10^{-2})(7.2 \times 10^{-3})} \\ = 0.97 \times 10^{-2} (M)$$

or

$$\text{pH} = 2.01.$$

where K_a (1.3×10^{-2}) is the acidic constant of H_2SO_3 in water. It was observed that the pH of a PSBT latex right after a bottle polymerization (where the SO_2 could not be released) was ~ 2.5 . If the latex in the bottle was purged with nitrogen gas for several minutes, or left in storage for a longer period of time, the SO_2 gas was released and the pH would rise to $\sim 5-6$.

The latex pH was adjusted with an aqueous NaHCO_3 solution and the percent NCO in the films prepared from the latices with different pH values was monitored by FTIR as a function of time (Fig. 3). The results indicate little effect of pH on the TMI stability and the loss of TMI due to hydrolysis in the latices was $<10\%$ after 30 days' storage at room temperature.

Shelf Stability of Latex Blend

A PSBT/PBD- NH_2 latex blend was made by mixing 20.00 g PSBT latex (30.74% solids, 2% TMI based on monomers, SLS surfactant) and 5.19 g PBD- NH_2 artificial latex (24.7% solids, SLS surfactant). The TMI/ NH_2 mole ratio in this blend was 0.64/1.0. The stability of this PSBT/PBD- NH_2 latex blend was examined in an accelerated aging process by keeping this blend in an oven at 50°C for 30 days. For comparison, the PSBT latex was studied in parallel. Both latices showed no observable coagulum formation.

The viscosities of the PSBT latex and the PSBT/PBD- NH_2 latex blend were measured as a function of shear rate. Shear thinning was observed in both cases, which is expected for polymer latices. Both the PSBT latex and the PSBT/PBD- NH_2 latex blend exhibited no significant viscosity change after 30 days' storage at 50°C . Figure 4(a) shows the results obtained for the PSBT/PBD- NH_2 latex blend. In addition, the particle size distribution determined by CHDF before and after the 30 days' storage at 50°C did not show any apparent change either, as can be seen in Figure 4(b).

All the above evidence shows that during the 30 days' storage at 50°C there was no observable coagulation in the latex blend, which would have resulted in increase in particle size and decrease in latex viscosity.

Further characterization of the storage stability of the latex blend was accomplished by measuring the PSBT/PBD- NH_2 latex stress-strain behavior and the solvent swelling behavior of

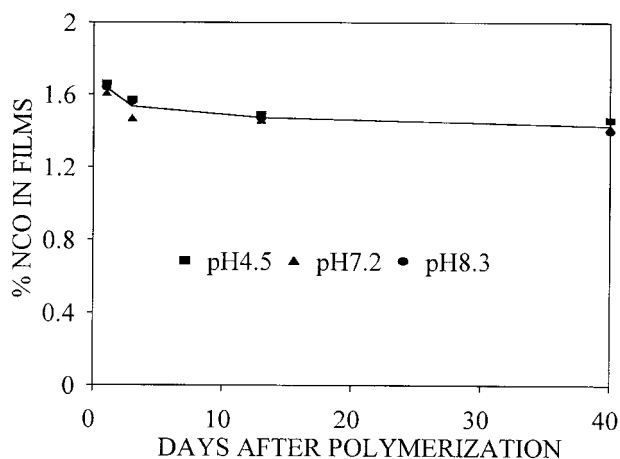


Figure 3 Percent NCO in the films prepared from the PSBT latexes at different pH values as a function of the latex storage time.

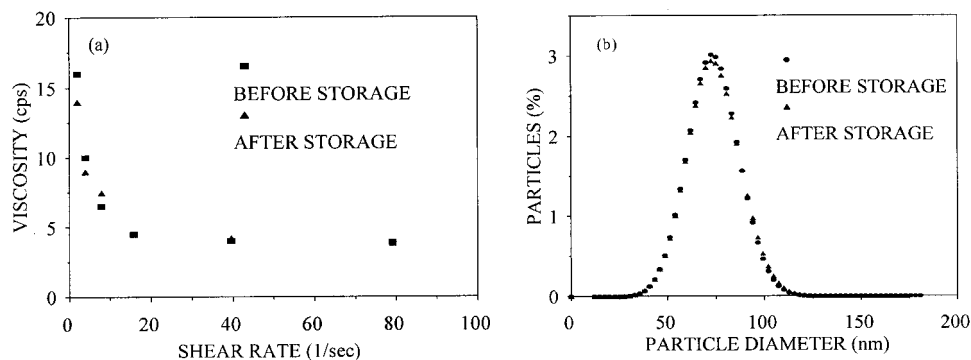


Figure 4 Viscosity as a function of shear rate (a) and the particle size weight distribution (b) of the PSBT/PBD-NH₂ latex blend (PSBT/PBD = 5.9) before and after 30 days storage at 50°C.

films prepared from the blend. Few changes were observed in the film mechanical strength and the solvent swelling ratio, as illustrated in Figure 5 and Table V. The stability of the latex blend was apparently due to the disperse nature of the latex in which the isocyanate-containing particles and the curing agent-containing particles had little chance to contact each other.

Effect of Telechelic Functionality on Crosslinking

Crosslinking was expected during film formation from the PSBT/PBD-NH₂ latex blend due to the reaction between the isocyanate groups of the PSBT latex and the amino groups in the PBD-NH₂ latex. In order to check the effect of the functionality of the telechelic PBD on the crosslinking,

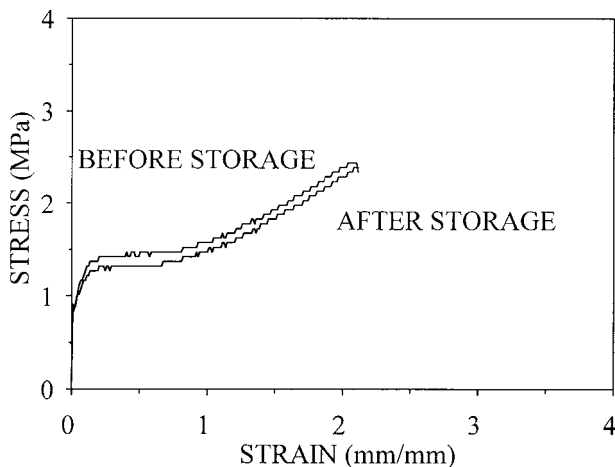


Figure 5 Stress-strain behavior of the PSBT/PBD-NH₂ film prepared from the latex blend, before and after the 30 days storage at 50°C.

three latex samples were prepared and cast into films: (1) PSBT latex; (2) PSBT/PBD-NH₂ latex blend; and (3) PSBT/PBD-CN latex blend (PBD-CN represents a cyanate-terminated telechelic PBD¹²; its artificial latex was prepared in the same way as the PBD-NH₂ latex). The PSBT/PBD-NH₂ and PSBT/PBD-CN weight ratios were 10 : 1. When each of the three latices were cast onto glass plates and air-dried for 42 h, three transparent films of ~ 0.4 mm thickness were obtained. By cutting a 10 × 3 mm piece from each of the three films and placing them separately into toluene for 24 h, it was observed that the PSBT and the PSBT/PBD-CN films dissolved completely while the PSBT/PBD-NH₂ film did not dissolve, but was only swollen. This indicated that while the PSBT film and the PSBT/PBD-CN film were not crosslinked, the PSBT/PBD-NH₂ film was certainly crosslinked.

The above experiment showed that while a cyanate functional group is not reactive toward an isocyanate group, the amino group is quite reactive. The reactivity of different functional groups towards isocyanates varies and depends on the specific isocyanate chemical structure.

Table V Properties of Films Prepared from the PSBT/PBD-NH₂ Latex Blend Before and After 30 Days' Storage at 50°C

	Modulus (MPa)	Toughness (MPa)	Strain (%)	Swelling Ratio (w/w_0)
Before storage	144	3.53	211	5.4
After storage	126	3.47	218	5.9

Table VI Gelation Time of PSBT Solutions with Different Curing Agents

	HDA	PBD-NH ₂	PBD-OH	PBD-COOH	PBD-OH + A ^a	PBD-OH + A + B ^a
Gel time	2 min	2 min	— ^b	— ^b	5 days	3 days

^a A = dibutyltin dilaurate; B = triethylamine.

^b No gelation noticed after 30 days.

The reactivities of amino, hydroxyl, and carboxyl groups toward the TMI isocyanate have not been reported up to this time. In the following experiments, the relative reactivity of these groups with TMI was studied in solution, thus eliminating the chain diffusion effect since the mixing of polymer chains in dilute solution is considered to be nearly instantaneous. The

PSBT dry polymer and the curing agent (PBD's with various functional groups) were dissolved in toluene separately before mixing them in a 1 : 2 TMI/NH₂ or TMI/OH mole ratio. The PSBT concentration after mixing was 1.5% in toluene. After mixing, the time when visually noticeable gelation was observed was considered as the "gel time." The results are shown in Table VI.

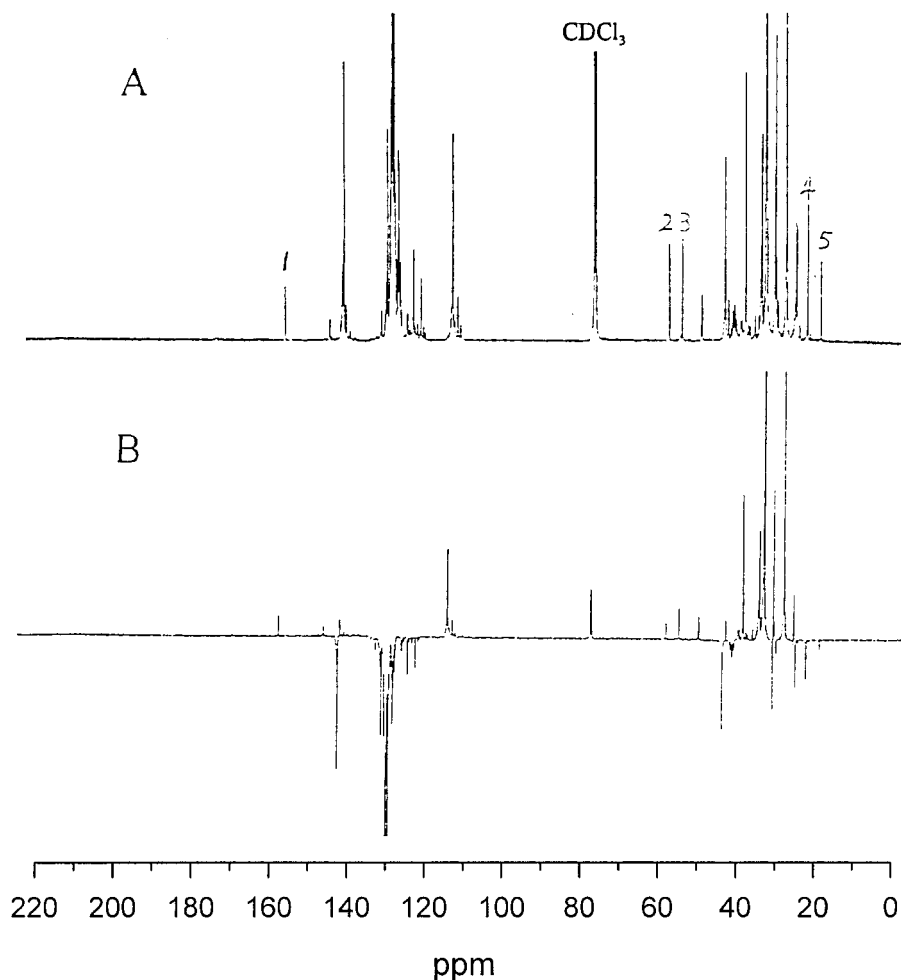


Figure 6 ¹³C-NMR (A) and its APT (B) spectra of TMI-terminated PBD. The signal at 158 ppm (1) is due to the urea carbon, —NH—C—NH—. Other signals for the carbons at the chain ends are tentatively assigned as: (2) Φ —C(CH₃)₂—NH—, (3) —NH—CH₂— $\sim\sim\sim$, (4) CH₂=C(CH₃)— Φ , (5) Φ —C(CH₃)₂—NH—.

Table VII Characteristics of the 1,12-Diaminedodecane (DAD) Artificial "Latex"

% Solids	DAD (mol)/latex (g)	Surfactant	Particle Size (nm) (CHDF)					
			D_n	D_w	PDI	D_v	f_{NH_2}	M_n
6.34	5.49×10^{-5}	SLS	63	74	1.17	67	2.0	200.37

PBD-COOH represents a carboxyl-terminated PBD¹² and PBD-OH a hydroxyl-terminated PBD (commercially available from Polyscience, Inc., $M_n = 2000$ g/mol). A short chain diamine, hexanediamine (HDA), was also tested as a crosslinking agent with the PSBT.

Gelation was almost instantaneous for the amino-terminated PBD and the hexanediamine, illustrating that the amino group was the most reactive toward the TMI isocyanate group. For the hydroxyl-terminated PBD to achieve any curing a catalyst (dibutyltin dilaurate) was needed. The catalysis was facilitated by a tertiary amine, triethylamine. Without the catalyst, the PBD-OH, like the PBD-COOH, could not cure the PSBT. It should be pointed out that the gelation times listed in Table VI only suggest that at the reported times the crosslinking had reached an extent such that the observable physical state of the system had changed. The actual crosslinking reaction might have begun much earlier. These results are consistent with

the general order of reactivity of isocyanates: amine > alcohol > carboxylic acid. The results also indicated that the TMI isocyanate is less reactive than most other isocyanates, since most isocyanates will crosslink with polyols with the aid of a catalyst in a much shorter time than 3 days.

Although use of PBD-OH is more economical than PBD-NH₂, its slow reaction with TMI would limit its application in this crosslinking study. In addition, the dibutyltin dilaurate and triethylamine catalyst not only catalyze the reaction of the TMI with the PBD-OH, but will also catalyze the reaction of TMI with water, the hydrolysis. This would complicate the crosslinking study of the latex film formation. For these reasons, the PBD-NH₂ was preferred in the present studies.

The crosslinking reaction of the TMI isocyanate with the PBD-NH₂ was further verified using ¹³C-NMR (Fig. 6). The reaction of TMI with the PBD-NH₂ was carried out in a THF solution. The crosslinking reaction is between the amino end-group in the PBD and the isocyanate group in the TMI:

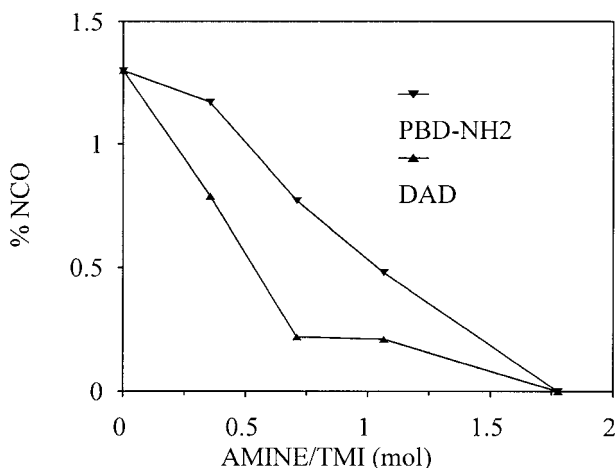
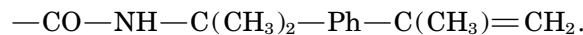
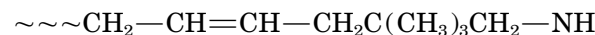
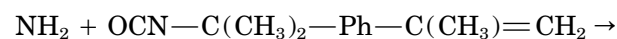
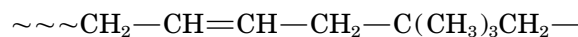


Figure 7 The effect of telechelic chain length on the variation in the %NCO as a function of the amine/TMI molar ratio in films cast from PSBT/PBD-NH₂ and PSBT/DAD latex blends, respectively. Films were dried at room temperature for 10 days.



The product showed a new signal at 158 ppm, which was assigned to the newly formed urea carbon ($-\text{NH}-\text{CO}-\text{NH}-$). The CH₂NH₂ signal at 52.4 ppm in the original PBD-NH₂ spectrum⁸ disappeared. No TMI signals were observed in Figure 6, indicating that any unreacted TMI was removed from the product by the purification. Thus the original amino-terminated PBD-NH₂ had been reacted to form TMI-terminated PBD-TMI with urea linkages.

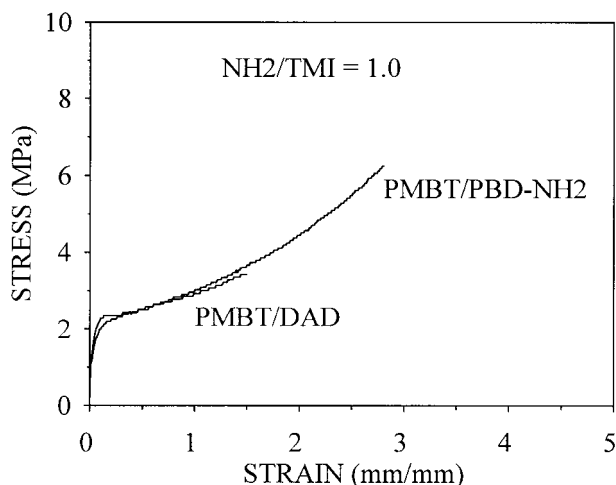


Figure 8 Stress–strain behavior of the PMBT/DAD film in comparison with the PMBT/PBD-NH₂ film; the NH₂/TMI mol ratio was 1.0 in both films.

Effect of Telechelic Chain Length on Crosslinking

Amino-terminated telechelic PBD's with chain lengths significantly different from each other were difficult to prepare. As an alternative, 1,12-diaminedodecane (DAD, MW = 200.37, Aldrich) was used, in order to compare its crosslinking behavior with the PBD-NH₂ (the hexanediamine, HDA, used in previous experiment was not used in the present study because it was not a good candidate for preparing an artificial latex due to its high water solubility).

The chain length of the telechelic PBD molecule could be calculated as follows. The PBD molecule contained 55% of 1,4-*trans*, 23% of 1,4-*cis*, and 22% of 1,2-vinyl units. The unit lengths were calculated to be: *trans* = 3.89 Å, *cis* = 2.86 Å, and vinyl = 1.54 Å. Thus the average unit length was 3.14 Å (55% · 3.89 + 23% · 2.86 + 22% · 1.54). A PBD molecule of molar mass 3100 g/mol contains 57 units. However, a fully stretched chain practically never exists. The random coil model for amorphous polymer chains gives the root-mean-square end-to-end distance to be $(\overline{r^2})^{1/2} = 3.14 \cdot \sqrt{57} = 24$ Å. The random coil model should not apply to a small molecule such as DAD. This linear molecule of 12 carbons with bond length of 1.54 Å should have a chain length near 10 Å.

An artificial “latex” of the DAD was prepared using the same method as for the amino-PBD latex. The DAD latex properties are listed in Table VII.

The consumption of isocyanates groups in films cast from PSBT/PBD-NH₂ and PSBT/DAD latex blends was studied. Blends with varying amino/TMI ratios were cast on FTIR disks and dried at room temperature for 10 days before FTIR spectra were taken of the films. The percent NCO in the films as a function of the amino/TMI molar ratio for both PSBT/DAD and PSBT/PBD-NH₂ films is shown in Figure 7. The consumption of the NCO in the PSBT/DAD films was greater than in the comparable PSBT/PBD-NH₂ films.

For the study of the mechanical properties of films made from the blends, a poly(methyl methacrylate/*n*-butyl acrylate/TMI) latex, poly(MMA/BA/TMI), designated PMBT, was used in place of the PSBT. The reason that MMA was used instead of St was that the PMBT resulted in more uniform (and more transparent) latex films from the latex blend, which allowed for better mechanical testing. The PMBT latex ($D_v = 77$ nm; PDI = 1.04 via CHDF) was synthesized in the same way as the PSBT latex. The solids content was 30%, the MMA/St mole ratio was 1 : 1, and the TMI was 2% by weight based on monomers.

Stress–strain measurements on the PMBT/DAD film showed a lower tensile strength at break and toughness than the PMBT/PBD-NH₂ film for the same NH₂/TMI ratio (Fig. 8). In a solvent swelling experiment, it turned out that although the PMBT/DAD film exhibited a lower swelling ratio than the PMBT/PBD-NH₂ film, it was more brittle and broke into pieces when removed from the toluene (Table VIII). While the lower swelling ratio indicates a higher degree of crosslinking, the brittleness might suggest the nature of the crosslinking to be predominantly intraparticle rather than interparticle.

CONCLUSIONS

The current results suggest that an ambient curable, isocyanated acrylic polymer with good

Table VIII Toluene Swelling Results for PMBT/DAD and PMBT/PBD-NH₂ Films at NH₂/TMI = 1.0 (Mole Ratio)

	Swelling Ratio W/W ₀	Film Characteristics
PMBT/ 1,12-diaminedodecane	4.9	Brittle
PMBT/PBD-NH ₂	6.0	Elastic

storage stability can be achieved via the latex blend approach. The hydrolysis of the isocyanate moiety is still a major limitation to long shelf life, although TMI is the most ideal candidate at the present time. However, the concept of the latex blend approach can be applied to other functionalized acrylic latex systems with more water-insensitive moieties than isocyanates.

The crosslinking of the isocyanate functional acrylic latex with the amino-telechelic polybutadiene was studied in terms of the effect of the type of functionality and telechelic chain length. It was found that only amino groups reacted with the TMI isocyanate at room temperature, without any added catalyst. For the telechelic crosslinker, a shorter chain length appears to allow easier diffusion into the acrylic particles, as indicated by a greater consumption of the isocyanate groups. However, the shorter chain crosslinker resulted in poorer films in terms of mechanical properties and solvent resistance, suggesting that intraparticle crosslinking was dominant over interparticle crosslinking.

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