Synthesis and Characterization of a Macromonomer Crosslinker

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ABSTRACT: A macromonomer crosslinker was synthesized by reacting an hydroxy-terminated ethylene–butylene diol copolymer with an excess of acrylic acid in toluene. ^{1}H-, ^{13}C-, and attached proton test (APT) NMR, Fourier transform IR, and gel permeation chromatography were used to characterize the macromonomer crosslinker. Its dilute solution behavior was also compared with the base diol. The addition of the ester moiety to the copolymer backbone did not involve any other side reactions, as evidenced by the similarities in the structures of the macromonomer crosslinker and the diol.
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INTRODUCTION

Macromonomers are macromolecular monomers of linear oligomeric or polymeric species having one or more polymerizable end groups. Such end groups can either be vinylic, acetylenic, acrylic, or heterocyclic. The use of macromonomers in polymerization reactions provides an alternative route to other methods previously used in the synthesis of copolymers. Many of the macromonomers are produced using free radical copolymerization for the synthesis of graft copolymers.[1–5] The alternative method (use of macromonomers) provides greater control and ease of incorporation for these graft copolymers, which cannot be easily obtained by conventional methods.

Core-shell monodisperse polystyrene latex particles functionalized for applications in immunology for binding with amino groups were recently synthesized using macromonomers. A two-step batch emulsion polymerization process[6] was utilized. Different types of functional groups could be incorporated into the macromonomer such as heterotelechelic poly(ethylene glycol) macromonomers possessing a methacrylol group at one end and a formyl group at the other end of the molecule,[7] or a methoxy and (p-vinylphenyl) butyl group in the macromonomer[8] depending on the end use. Complex tethered brush, star, and comb structures possessing reactive groups can also be prepared with additional control using macromonomers.[9–11] Similarly, controlled branching in amphiphilic polymers[12] brought about by the use of macromonomers was found to be useful in applications such as unimolecular micelles or associative thickeners. Branched achitectures promote the formation of monomolecular micelles, which gave better stability compared to linear structures. Advantages of macromonomer technology include accessibility for the design of well-defined microstructures with greater control of chain length and incorporation of the backbone or main chain, which make the macromonomers ideal species in many reaction systems including crosslinking reactions. This paper describes the details of the synthesis and characterization of a hydrophobic bifunctional macromonomer crosslinker.

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Table I Recipe Used for the Synthesis of the Macromonomer Crosslinker

Component	Ingredient	Wt/g
Reactants	Diol	87.0 (0.025 mol)
	Acrylic acid	7.2 (0.1 mol)
Solvent	Toluene	94.2
Catalyst	Triflic acid	0.81
Inhibitors	MHQ	0.126
	or (TBC)	0.126
	Nitrobenzene	0.0126
	Oxygen bubbled in	

EXPERIMENTAL PROCEDURES

Materials and Synthesis

The macromonomer crosslinker was synthesized by reacting a diol, which is a hydroxy- terminated ethylene-butylene copolymer (Shell Chemical Co.) with an excess of acrylic acid (Aldrich). The synthesis recipe is shown in Table I. This esterification reaction is catalyzed by the addition of trifloromethane sulfonic acid (triflic acid, Aldrich). Inhibitors such as methyl hydroquinone (MHQ), nitrobenzene and t-butyl catechol (TBC; all obtained from Aldrich) were utilized to prevent the double bonds associated with the acrylic acid moiety from polymerizing during the synthesis of the macromonomer crosslinker.

The diol has a molecular weight of ~3500 g/mol and a neat viscosity of 50,000 cps at 25°C; hence, dilution with toluene was first carried out before charging the diol to the reactor. The inhibitors were added to the reactor followed by the addition of the acrylic acid. Oxygen, which is also an inhibitor,[13] was gently bubbled through the reaction mixture. The reaction mixture was kept continuously stirred. The temperature of the reaction mixture was raised to 50°C by means of a thermostated heating mantle, after which the catalyst, triflic acid was added. The reactor was then sealed and the mixture was heated to 115°C. At this temperature, the azeotropic mixture of toluene and the water, which resulted from the addition of the acrylic acid to the ethylene–butylene diol copolymer, was collected in the receiver arm. Depending on the heating rate, 80–90% of the theoretical amount of water expected based on the reaction scheme in Figure 1 was accumulated within 2 h of heating. When no further increase in amount of water was collected, the reaction mixture was cooled down to room temperature.

Purification

Acrylic acid (0.1 mole) was used in excess of the diol copolymer (0.025 mole); hence, there would be unreacted acrylic acid present in the product. The product must also be purified from the catalyst as well as the inhibitors used. Two purification processes were utilized to obtain the macromonomer crosslinker. The first involved the addition of 2 wt % aqueous sodium hydroxide (NaOH) solution at equal volumes to the cooled reaction mixture, which had been placed in a separatory funnel. This was followed with several exchanges of aqueous solution of sodium hydroxide solution at pH 11. Finally, extensive washing with deionized water was carried out. Second, as opposed to the purification stages for aqueous NaOH solution, a solid phase of a less basic alkali, i.e., sodium bicarbonate, was used. The repeated use (at least 4 times) of sodium bicarbonate to purify the reaction mixture eliminated the need to deal with the formation of an emulsion when aqueous sodium hydroxide was added to the reaction mixture. The amount of bicarbonate used was about the same volume as the reaction mixture. This mixture (bicarbonate and reaction mixture) was stirred for at least 24 h before it was allowed to settle. After repeated treatment with the sodium bicarbonate, the macromonomer crosslinker was then separated and filtered, followed by drying under vacuum after it was purified.

CHARACTERIZATION OF THE MACROMONOMER CROSSLINKER

The reaction scheme for the macromonomer crosslinker is summarized in Figure 1. The structure of the macromonomer crosslinker was determined using high-resolution ^1H nuclear magnetic resonance (NMR) spectroscopy (500 MHz, Aspect

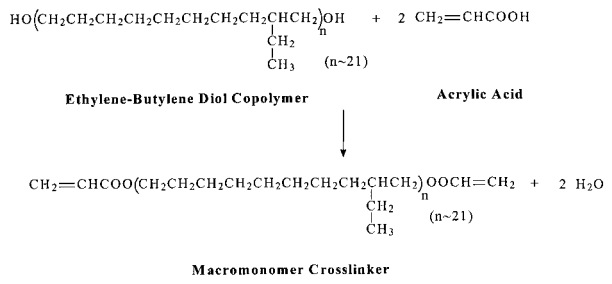

Figure 1 Reaction scheme for the synthesis of the macromonomer crosslinker.

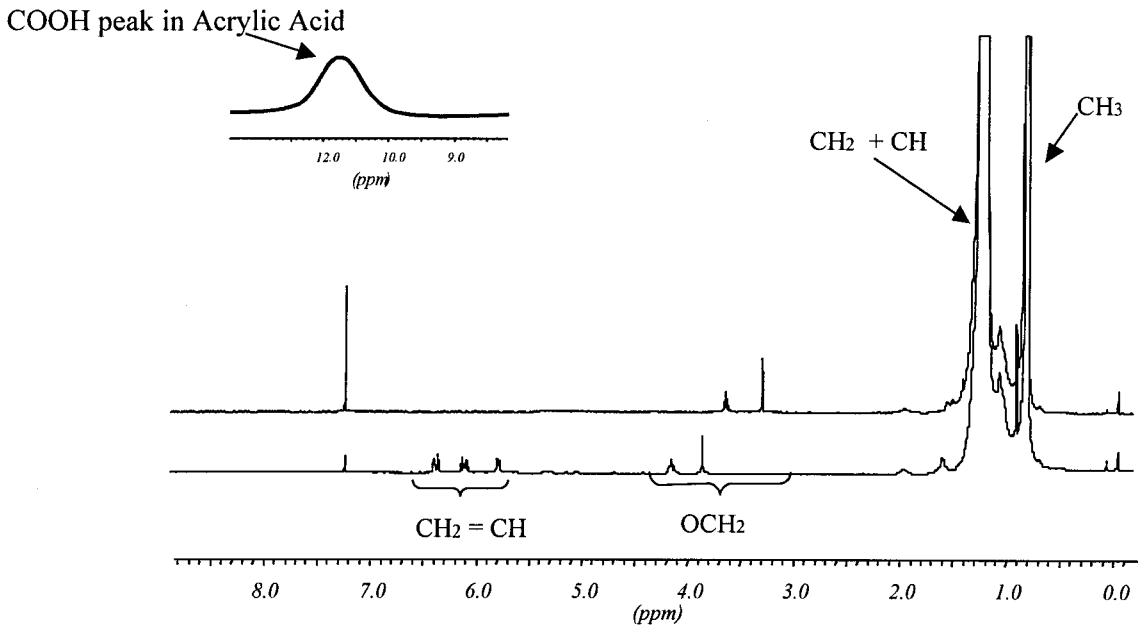

Figure 2 ^{1}H-NMR spectra of the base diol (top) and the macromonomer crosslinker (bottom). The insert shows the characteristic peak of carboxylic acid (COOH) found at 11.7 ppm; this peak was not present in the macromonomer crosslinker.

3000, Bruker). The proton NMR measurements utilized a relaxation time of 3 s, and 400 scans were carried out for each sample. Three to ten wt % macromonomer crosslinker and diol solutions were prepared in deuterated chloroform for the NMR measurements. The chemical shift for the impurity ($CHCl_3$) associated with the deuterated chloroform occurred at 7.24 ppm.[14] Figure 2 shows the spectra obtained for the macromonomer crosslinker and the diol in deuterated chloroform.

The methyl protons (CH_3) are not influenced by other neighboring protons; hence, the proton peak associated with the methyl group will be clearly separated and easily discernible in the spectrum. Since the methyl groups do not participate in any chemical reactions, the methyl proton peak can be used as an internal standard. This methyl peak is found at 0.7–0.9 ppm for both the macromonomer crosslinker and the diol. The integral of this peak would represent the three methyl protons, and hence a value for a single proton can be found. The three protons associated with the double bonds (CH_2═CH) are found in the region between 5.6 and 6.6 ppm in the macromonomer crosslinker spectrum. Each gave rise to a peak indicating that these protons are not chemically equivalent. An analysis can be carried out using the $OCOCH_2$ proton peaks, which are found between 3.7 and 4.3 ppm. These peaks are also not expected to react during the macromonomer crosslinker synthesis. The protons of the $OCOCH_2$ groups are observed as two nonchemically equivalent peaks in the NMR spectrum of the macromonomer crosslinker. These protons can also be observed in the diol spectrum. However, the chemical shifts for the $HOCH_2$ groups in the diol are found upfield, i.e., 3.2–3.7 ppm; hence, this is the crucial evidence that clearly confirms the formation of the macromonomer crosslinker as a product in contrast to the diol, the principal reactant. The presence of another oxygen atom in the vicinity of the $OCOCH_2$ groups explains the chemical shift of the $OCOCH_2$ groups ($OCOH_2$—ester) found downfield for the macromonomer crosslinker. The absence of any significant peaks at 3.2–3.7 ppm in the macromonomer crosslinker suggests that the diol had been completely converted into the macromonomer crosslinker. The absence of the other principal reactant, acrylic acid, is indicated by the absence of a carboxylic acid peak (COOH), which otherwise should be observed at 11–11.5 ppm in the ^{1}H-NMR spectrum of the acrylic acid. The comparison of methyl protons, $HOCH_2$ and $OCOCH_2$ protons of the diol, and the macromonomer crosslinker, respectively, provided additional evidence for the preservation of the double bonds during the synthesis of the macromonomer; i.e., 3

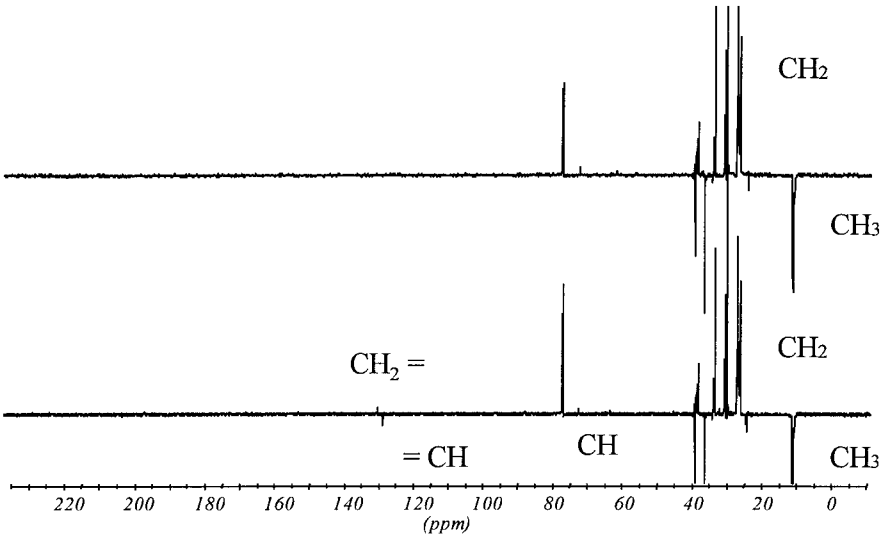

Figure 3 APT-NMR spectra of the diol (top) and the macromonomer crosslinker (bottom). Both spectra are very similar except for the CH_2═CH group present in the macromonomer crosslinker. The carbonyl group C═O cannot be easily observed because it is very small and is obscured by the baseline. The methyl carbon (CH_3) and the methine carbon groups (CH) point downward, and the methylene carbon (CH_2) and quaternary carbon (C) groups point upward.

protons of the CH_2—CH corresponded to 2 protons of the $OCOCH_2$.

Further elucidation of the macromonomer crosslinker structure was made possible by the use of one-dimensional attached proton test (APT) NMR, a decoupled ^{13}C-NMR technique that discriminates between the number of protons attached to the carbon atom by type and provides information as to the ^{1}H—^{13}C connectivity. The methine protons (CH) were not easily observable from the ^{1}H-NMR spectra of the macromonomer crosslinker or the diol. Figure 3 shows the APT spectra of the diol and the macromonomer crosslinker. These were measured with a relaxation time of 6 s and a total of 6000 scans. The methyl and methine peaks are those peaks which point downward. The methylene and the quaternary carbon peaks are those pointing upward. The deuterated chloroform peak gave rise to peaks pointing downward due to the quaternary carbon. Clearly, the APT spectrum of the macromonomer crosslinker and the diol are very similar except for the presence of the CH_2═CH double bond peaks in the macromonomer crosslinker at 127–131 ppm. A line broadening of 3 was applied. Methine peaks are clearly present in at least three different environments; since they were not observed in the ^{1}H-NMR spectra, they must be buried under the huge peak at about 1.0–1.9 ppm. The expanded APT NMR regions between 25 and 42 ppm of the diol and the macromonomer crosslinker where most of the methylene carbons (CH_2) and the methine carbons (CH) of the backbone chains are located is shown in Figure 4; there appears to be little structural differences between the diol and the macromonomer crosslinker.

The ^{13}C-NMR spectra of the macromonomer crosslinker and the diol were also acquired under the same conditions as in the APT measurements, and are shown in Figure 5. The carbonyl peak (166 ppm) and the double bond peaks (at about 130 ppm) associated with the macromonomer crosslinker can be clearly identified, and were absent as expected in the diol.

Fourier transform infrared (FTIR) spectroscopy (Matteson Polaris Spectrometer) also was utilized to determine the structure of the reactants (diol and acrylic acid) and the product (macromonomer crosslinker). The data was obtained at a resolution of 4 cm^{-1}, signal gain of 2, and a total of 64 scans. The detector used was a large mercury cadmium telluride/triglycine sulfate (MCT/TGS) with 25% of iris opening. Figure 6 shows the FTIR spectra of the acrylic acid monomer and the diol. These were compared with the spectra obtained from the macromonomer crosslinker. The acrylic acid spectrum provided

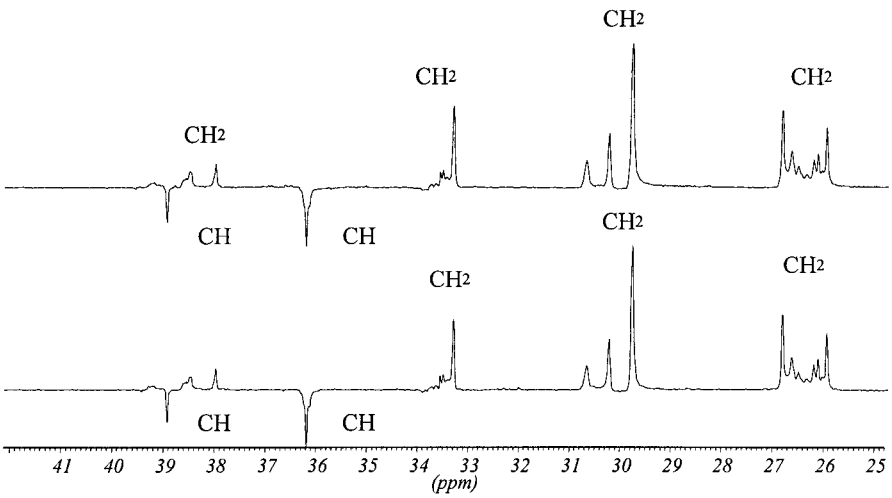

Figure 4 Expanded regions (25–42 ppm) of the APT-NMR spectra of the diol (top) and macromonomer crosslinker (bottom). The methylene carbons (CH_2) and the methine carbons (CH) of the main backbone chain are primarily found in this region.

the absorbance profile for the COOH group, a huge broad peak centered about 3200 cm^{-1}, that is clearly absent in the macromonomer crosslinker. The huge peak observed at 2900 cm^{-1} in the macromonomer crosslinker is also seen in the diol. This peak is made up of the stretching of the carbon–hydrogen bonds. The CH_2═CH double bond peak occurs at 1636 cm^{-1} in the acrylic acid and was also observed in the macromonomer crosslinker spectrum at the same wavenumber. The most convincing confirmation for the formation of the macromonomer crosslinker product comes from the carbonyl group absorbance (C═O), which should differ in the acrylic acid and in the macromonomer crosslinker because one is an acid and the other is an ester. The C═O peak absorbance was seen at 1706 cm^{-1} in the acrylic acid and at 1732 cm^{-1} in the macromonomer crosslinker. The diol does not exhibit any of the carbonyl or the double bond peaks. The characteristic peak of the alcohol group (OH) associated with the diol at 3300 cm^{-1} was not observed in the FTIR spectrum of the macromonomer crosslinker, as expected.

The effectiveness of the inhibitors and the purification techniques employed were also evaluated using ^{1}H-NMR spectroscopy. Table II shows a comparison of the ratios of the areas under the

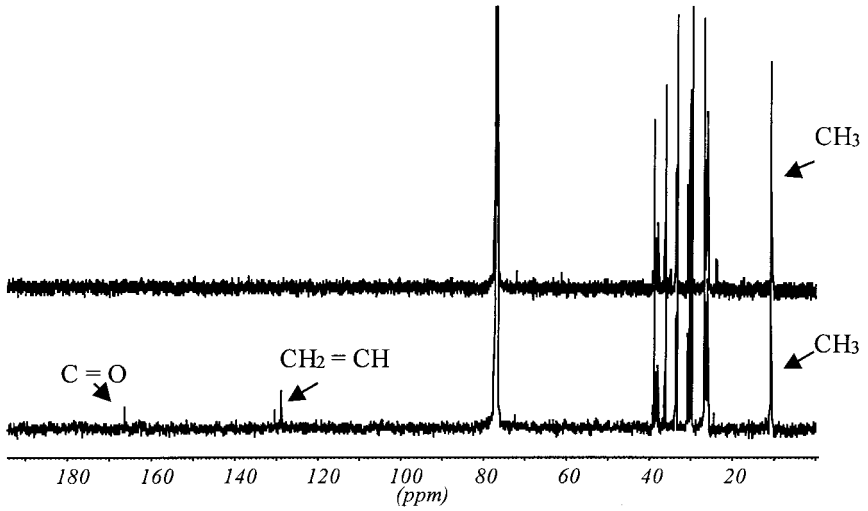

Figure 5 ^{13}C-NMR spectra of diol (top) and macromonomer crosslinker (bottom).

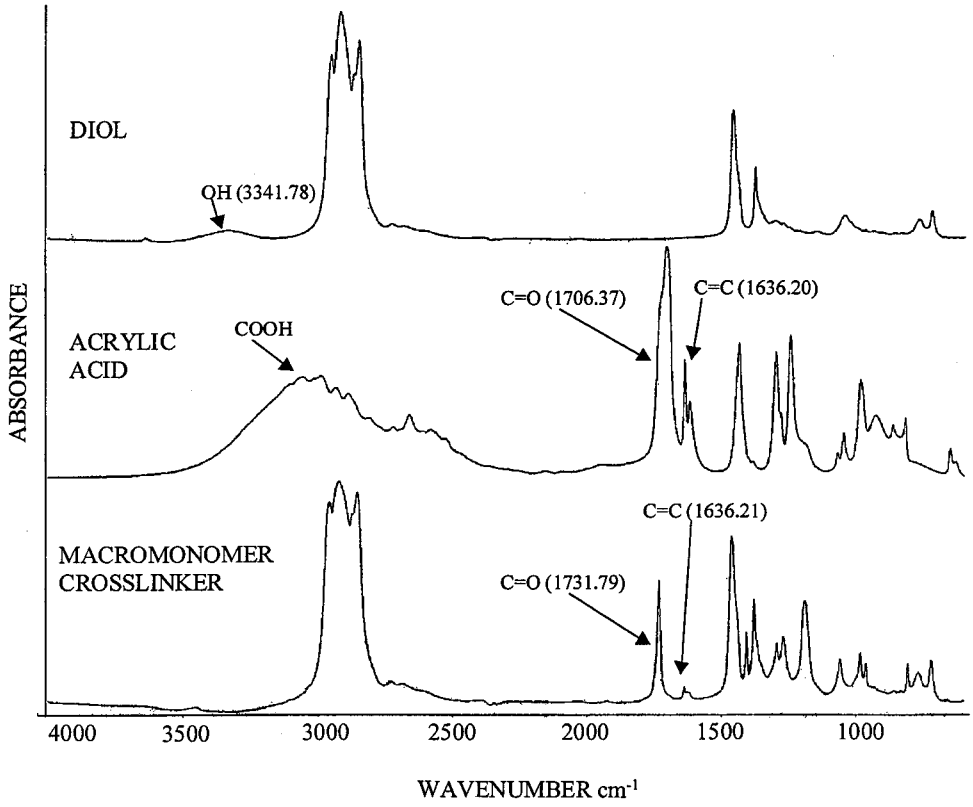

Figure 6 FTIR Spectra of diol, acrylic acid, and the macromonomer crosslinker.

peaks of CH_2═CH to CH_3 for the different macromonomer crosslinkers prepared with different inhibitor systems and with different purification procedures. The similarities in the ratios obtained for all the inhibitor systems suggest that the inhibitors employed were effective in preventing the polymerization of the double bonds during the synthesis of the macromonomer crosslinker, and that both purification systems were as effective.

The dilute solution behavior of the macromonomer crosslinker was compared with the base diol. Using the Huggin[15] and Kraemer[16] equations, the reduced viscosity [η_{sp}/C] and inherent viscosity [η_r/C], were calculated from the measured efflux time of several concentrations of the macromonomer crosslinker and the diol in tetrahydrofuran (THF) at room temperature (20°C), to give the intrinsic viscosity [η] by extrapolation to zero concentration.[17] Table III lists the intrinsic viscosity [η] for macromonomer crosslinker 1 and 2 (has twice the amount of inhibitor as 1), as well as the diol. The intrinsic viscosity for the macromonomer crosslinker 1 and 2 are very similar. Their intrinsic viscosities were also similar to the intrinsic viscosity of the diol, as is expected.

Table II Comparison of the Ratios of the Integrals of the Double Bond Peaks to the Integral of the Methyl Peak Obtained from ^{1}H-NMR Spectroscopic Measurements and Analysis

Purification Procedure and Inhibitor	CH_2═CH/CH_3
Solid $NaHCO_3$ (TBC)	0.054
Aqueous NaOH (TBC)	0.053
Solid $NaHCO_3$ (MHQ)	0.051
Aqueous NaOH (MHQ)	0.050

Table III Dilute Solution Measurements (Intrinsic Viscosity) of Diol and Macromonomer Crosslinker

Sample	[η] (dL/g)
Diol	0.12
Macromonomer Crosslinker (1)	0.13
Macromonomer Crosslinker (2)	0.13

Table IV Molecular Weight Averages of Diol, Macromonomer Crosslinker, and Polybutadiene Standards

Sample	M_n (g/mol)	M_w (g/mol)
Diol	3350 ± 150	3950 ± 50
Macromonomer Crosslinker	3300 + 100	4100 ± 100
PB 3400	3214	6661
PB 2600	2351	7135

Gel permeation chromatography (GPC; Waters Associates) was used for the determination of the molecular weight of the macromonomer crosslinker and the diol. Polybutadiene standards were used with universal parameters for the calibration curve. All solutions (1 wt %) were prepared in THF. Table IV summarizes the molecular weight averages obtained from the GPC measurements of the macromonomer crosslinker, diol, and two other polybutadiene standards (PB3400 and PB 2600). The latter were included to ascertain the accuracy of the measurements. The numbers associated with the standards reflect their molecular weights, i.e., 3400 and 2600 g/mol, respectively. Shell Chemical Company reported the molecular weight of the diol as 3480 $gmol^{-1}$, which is very close to the molecular weight of the diol obtained from the GPC measurements found here.

The similarities in the average molecular weights and the conservation of the polydispersity index of the macromonomer crosslinker in comparison with the diol is a good indicator that the synthesis of the macromonomer crosslinker did not involve any other side reactions such as dehydration of the diol, β-scission of the ester, or branching and crosslinking. The presence of side reactions would lead to changes in molecular weights of the product.

CONCLUSIONS

A macromonomer crosslinker was synthesized by the reaction of a hydroxy-terminated ethylene–butylene diol copolymer with an excess of acrylic acid. The addition of the ester moiety to the ethylene–butylene chain did not involve other side reactions as evidenced by the similarities in structural details from ^{1}H-, ^{13}C-, and APT-NMR measurements, molecular weight determination by GPC, and similar dilute solution behavior of the diol and the resulting macromonomer crosslinker. Structural details were also obtained from FTIR spectroscopy for confirmation of the characteristic groups.

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