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Smart "All Acrylate" ABA Triblock Copolymer Bearing Reactive Functionality via Atom Transfer Radical Polymerization (ATRP): Demonstration of a "Click Reaction" in Thermoreversible Property

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ABSTRACT: Tailor-made ABA triblock copolymers (poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF)) bearing a reactive pendant furfuryl group were successfully synthesized by atom transfer radical polymerization. The chemical compositions were calculated by ^{1}H NMR, and molecular weights and molecular weight distributions were determined by gel permeation chromatography analysis. The tensile properties of the triblock copolymers such as tensile strength, elongation at break, and tension set were studied. Differential scanning calorimetry (DSC) analysis and dynamic mechanical analysis (DMA) show the existence of two glass transition temperatures (T_g) and thereby the presence of well-defined soft and hard phase. Thermoreversible self-healing material was successfully prepared by using Diels–Alder reaction between this reactive furfuryl group (diene) of the ABA triblock copolymer and a bismaleimide (dienophile). Thermoreversible property of the polymer was confirmed by FTIR and DSC analysis. The self-healing nature of the polymers was characterized by scanning electronic microscopic analysis. Viscoelastic behavior of the Diels–Alder polymer was thoroughly studied by DMA studies.

Introduction

In recent years, there has been great interest to design and to synthesize newer types of polymeric materials, with unique properties to meet with demands and challenges for novel applications.[1] Smart polymers[2−5] are the materials which can respond toward external stimuli like the change of temperature, light, magnetic field, and electric field. Because of their interesting properties, they are used in self-healing or self-repairing materials, in novel biomaterial for biomedical applications, in microelectronic applications, and in different strategic applications like in shape memory polymers.[2−4] The self-healing concept involves the development of a new class of cross-linked polymer capable of healing internal cracks through thermoreversible covalent bonds. The concept of self-healing polymeric materials was proposed in the 1980s[6] as a means of healing invisible microcracks for extending the service life and safety of the polymeric components. Recently, there are literatures which report that the self-healing polymeric materials have the built-in capability to substantially recover their load transferring ability after damage. Such recovery can occur separately or by activation with heat or radiation. Self-healing polymers are finding applications in scratch resistance coatings and in repairing the cracks developed in a material.[7] Smart materials are expected to contribute greatly to the safety and durability of polymeric components without high costs of active monitoring or external repair.[2−5]

Homo- and copolymers of furfuryl methacrylate (FMA) are interesting materials because of the presence of reactive furfuryl functionality.[8−11] This reactive diene functionality can be used for the Diels–Alder (DA) reaction using a suitable bismaleimide (BM) as dienophile. DA reaction is an interesting "click reaction". The concept "click chemistry" was coined by K. B. Sharpless, who was awarded the Nobel Prize in 2001,[12] because of his outstanding contribution in this field. Use of "click chemistry" nowadays has become a powerful tool to design tailor-made polymer architectures.[13] Kyeremateng et al.[14] reported the click reaction of 1,3 dipolar cycloaddition reaction between azido-terminated AB diblock copolymer and α-alkyne fluorinated compound. Opsteen et al.[15] demonstrated the combination of ATRP with click reaction of Cu(I)-catalyzed azide–alkyne cycloaddition for the modular synthesis of block copolymers. The DA click reaction is a very versatile, efficient, and environment-friendly process. This reaction occurs at very high yield and at relatively simple reaction condition in no solvent or in benign solvent. Importantly, DA reaction can be made thermoreversible via the retro-DA (rDA) reaction. It is very challenging to prepare ABA triblock copolymers bearing reactive functionality (e.g., furfuryl functionality group)[16] because of the several side reactions involving reactive diene during the polymerization of this functional monomer.[8−11] The preparation of well-defined reversible functional triblock copolymers is an active field of research because of their applications in the thermoplastic elastomers (TPE),[17−19] self-healing polymers,[20,21] and biomedical applications.[22,23] TPEs are a family of polymers that can be repeatedly stretched without permanently deforming the shape of the material.[24,25] ABA triblock copolymers composed of an elastomeric middle block (B block) and glassy end blocks (A block) can act as TPE. The glassy microdomains act as physical or chemical cross-links. It can also act as reinforcing filler rendering attractive thermal and mechanical properties without vulcanization and without addition of any filler extraneously.[26]

Block copolymers based on styrene (e.g., SBS, SEBS, etc.) and based on acrylates (e.g., PMMA–PBA–PMMA) are useful TPEs and are prepared by anionic polymerization. Ionic polymerizations are very much susceptible to impurities present in the monomer, solvents, and the initiator.[26] Controlled radical

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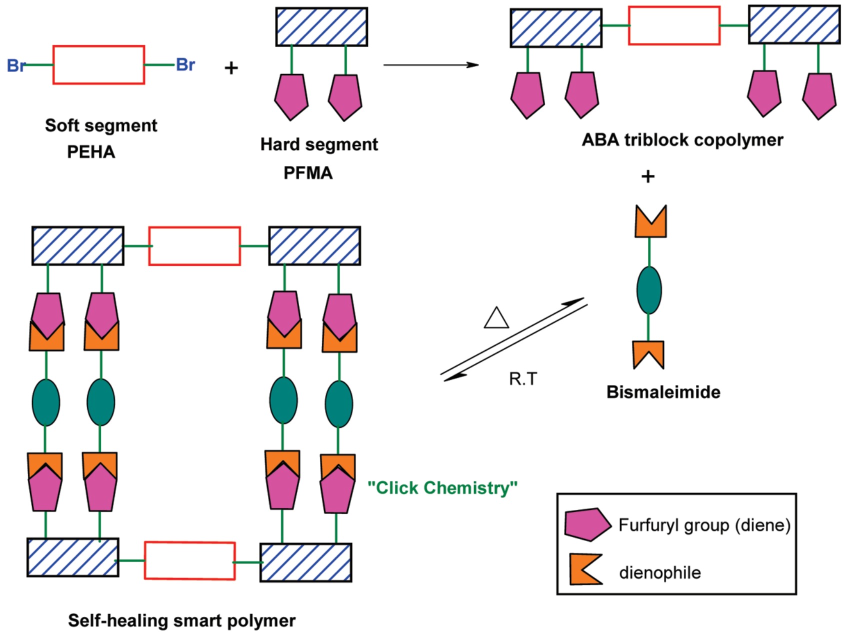
Scheme 1. General Presentation of Self-Healing ABA Triblock Polymer by Diels−Alder "Click Chemistry"



polymerizations (CRP) have several advantages over ionic polymerization. It eliminates the stringent reaction of ionic polymerization but maintains versatility of ionic polymerization. Among different types of CRP, transition metal halide-catalyzed CRP, widely known as atom transfer radical polymerization (ATRP), is widely used to prepare different tailor-made polymers with complex architectures like block copolymers, star polymers, hyperbranched polymers, etc.[27−29] Interestingly, ATRP can be applied to a great variety of monomers, especially functional monomers which are very difficult to polymerize via ionic polymerizations. ATRP has been used to prepare different block copolymers based on acrylates.[30] Recently, we have reported ATRP of furfuryl-containing monomers and studied the DA reaction in the resultant polymers.[31] Preparation of well-defined block copolymer with controlled block length is very challenging, especially because of the presence of the reactive furfuryl functionality.

To the best of our knowledge use of click chemistry of DA reaction is not explored in the tailor-made block copolymer bearing reactive functionality prepared by any method of controlled radical polymerization. The objective of this present work is to prepare tailor-made thermoreversible ABA triblock copolymers (PFMA-*b*-PEHA-*b*-PFMA) bearing reactive furfuryl functionality with controlled molecular weight via ATRP and to apply this polymer in DA and retro-DA reaction by using bismaleimide as dienophile. In this 2-ethylhexyl acrylate (EHA) was used as a middle block. PEHA has very low T_g (−58 °C), and it has very good film formation properties. It is a useful component for paints, coatings, and adhesive applications.[32] The synthetic outline of this investigation is shown in Scheme 1. In this triblock copolymer PFMA block (T_g = +65 °C) and PEHA (T_g = −50 °C) can act as hard and soft phase, respectively. Thermoreversible nature of the Diels−Alder block copolymers (i.e., block copolymer−bismaleimide adduct) was characterized by FTIR and by a heating−cooling cycle in differential scanning calorimetry (DSC). The thermal and mechanical properties of the polymers were characterized by thermogravimetric analysis and dynamic mechanical analysis. The self-healing nature of the triblock polymers is characterized by scanning electronic microscopic analysis (SEM) and differential scanning calorimetry analysis (DSC).

Experimental Section

Materials. Furfuryl methacrylate (FMA) (97%, Aldrich) and 2-ethylhexyl acrylate (EHA) (98%, Aldrich) were purified by vacuum distillation prior to use. CuCl and CuBr (98%, Aldrich) were purified by washing with glacial acetic acid, followed by diethyl ether, and then dried under vacuum. Toluene (SD Fine Chemicals, Mumbai, India) was purified by vacuum distillation over CaH_2. Triethylamine (TEA, SD Fine Chemicals, Mumbai, India) was dried over KOH and distilled before use. Dichloromethane (DCM, SD Fine Chemicals, Mumbai, India) was dried over anhydrous $CaCl_2$ and was distilled over anhydrous P_2O_5 before use. Ethylene glycol (99.8%), 2-bromoisobutyryl bromide (98%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%), 2,2′-bipyridine (bpy) (99%), and 1,1-(methylenedi-4,1-phenylene)bismaleimide (BM) were obtained from Aldrich and were used as received.

Instrumentation. *Nuclear Magnetic Resonance Spectroscopy* (*NMR*). ^{1}H NMR characterization of polymers was performed at room temperature (25 °C) with a Bruker 400-MHz spectrometer using $CDCl_3$ as solvent which had a small amount of tetramethylsilane (TMS) as internal standard.

FTIR Spectroscopy. FTIR spectra were recorded on a Perkin-Elmer, Inc., version 5.0.1 spectrophotometer. The polymer sample dissolved in chloroform was film cast over KBr cells, and then the IR spectra were recorded. The powder samples (Diels−Alder cross-linked polymer) were ground with spectroscopic grade KBr and made into pellets according to the specified sample preparation procedure. FTIR spectra were recorded in the range of 4000−400 cm^{-1}.

Gel Permeation Chromatography (*GPC*). GPC spectra were recorded on a Viscotek GPC equipped with a refractive index detector (model VE 3580) at ambient temperature. The polymer solution was passed through two ViscoGEL GPC columns (model GMHHR-M #17392) connected in series. The columns were mixed bed column having pore size of 30−650 Å and were suitable for the analysis of polymer of medium to high molecular weights (exclusion limit M_n = 1 × 10^6). Tetrahydrofuran (THF) was used as eluent at room temperature with a flow rate of 1.0 mL/min. Linear poly(methyl methacrylate) (PMMA) standards (Polymer Laboratories) were used as calibration standard. Data acquisition and processing were performed using Viscotek OMNI-01 software.

Scanning Electronic Microscopy (*SEM*). The self-healing nature of the triblock cross-linked polymer was studied using surface morphological images by JEOL JSM 850 scanning electron microscope (SEM). A deliberate scratch was made on the film surface and then placed at 120 °C for 4 h. The samples were taken at regular intervals for SEM imaging.

Tensile Measurements. Tensile properties such as ultimate tensile stress, elongation at break, and tensile modulus were determined using a Hounsfield 10KS Universal Testing Machine, U.K., at a cross-head speed of 50 mm/min as per ASTM standard D 412-98a. Dumbbell specimens were cut using ASTM Die C in a hydraulic cutting press and were used for the study.

Tension set was measured using a Hounsfield 10KS Universal Testing Machine, U.K., with a Die C dumbbell specimen. The sample was first clamped in the jaws and was subjected with a strain of 5% at a constant grip separation rate of 10 mm/min. The sample was kept under tension for 10 min. After that, the stress was removed and the sample kept for retraction. The elongation was measured 10 min after the testing. Tension set in percentage was calculated using the following equation:

$$\text{tension set (\%)} = \frac{\text{change in length after test}}{\text{original length}} \times 100$$

Differential Scanning Calorimetry (*DSC*). Differential scanning calorimetry analysis was performed in a TA DSC instrument (model Q100) at a temperature range of −100 to 200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. A sample weight of ~4 mg was taken for the measurements. The temperature against heat flow was recorded. The glass-transition temperature (T_g) was calculated from the second scan to ensure reproducible thermograms. The baseline was calibrated by scanning the temperature domain of the experiments with an empty pan. The enthalpy was calibrated with an indium standard as well as the heat capacity was calibrated by measuring with sapphire disk supplied by TA Instruments. The temperature calibration was performed with different metal standards at the various heating rates.

Dynamic Mechanical Analysis (*DMA*)

Temperature Sweep. Dynamic mechanical properties were measured using a dynamic mechanical analyzer (DMA 2980, TA Instruments). The temperature sweep experiments were carried out from −100 to +200 °C at a heating rate of 2 °C/min using a tension film clamp keeping a constant frequency of 1 Hz and oscillating amplitude of 20 μm.

Frequency Sweep. Frequency dependency of DA cross-linked polymer on dynamic mechanical properties such as storage modulus (E'), loss modulus, damping factor (tan δ), and dynamic viscosity were studied by performing a frequency sweep test. The tests were carried out using a compression mode clamp with a frequency range from 0.1 to 50 Hz keeping isothermal condition and oscillating amplitude of 20 μm. Tests were performed at five different temperatures ±40 °C from the temperature for cleavage of DA cross-links.

Synthesis. *Synthesis of Difunctional Initiator 1,2-Bis*(*bromoisobutyryloxy*)*ethane* (*BBiBE*). Ethylene glycol (2.00 g, 3.22×10^{-2} mol), 50 mL of dry dichloromethane, and dry triethylamine (6.49 g, 6.43×10^{-2} mol) were placed in a 250 mL three-necked round-bottom flask and were cooled below 5 °C. Then 2-bromoisobutyryl bromide (14.80 g, 6.44×10^{-2} mol) was added dropwise under a nitrogen atmosphere with constant stirring. The reaction was continued at 5 °C for 1 h. After 1 h, the ice bath was removed and the mixture was stirred overnight at room temperature. The reaction mixture was washed with distilled water and was extracted with dichloromethane. The organic layer was washed with $NaHCO_3$ and then with brine solution and finally was dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated using a rotary evaporator which yielded white crystalline solid. The final product was recrystallized from methanol, and the resultant product was white needlelike crystal. Yield: 12.45 g (80%). ^{1}H NMR: δ = 1.94 ($-CH_3$) and 3.72 ppm (d, 2H, $-OCH_2$). ^{13}C NMR: δ = 56.35 ($-OCH_2$), 75.86 (C−Br), and 171.01 ppm (⟩C=O).

Synthesis of α,ω-Dibromo-poly(*2-ethylhexyl acrylate*) *Macroinitiator by ATRP* (*Br−PEHA−Br*). CuBr (0.034 g, 2.41×10^{-4} mol) and bipyridine (0.037 g, 2.41×10^{-4} mol) were taken in a 100 mL three-necked round-bottom flask. The monomer, 2-ethylhexyl acrylate (5.00 g, 2.71×10^{-2} mol), was then added. The flask was sealed with a condenser in one neck and a silicon rubber septum in the other. The polymerization was carried out under a nitrogen atmosphere. The difunctional initiator 1, 2-bis(bromoisobutyryloxy)ethane (BBiBE) (0.086 g, 2.41×10^{-4} mol) was dissolved in 1 mL of THF. The polymerization was started after addition of the solution of difunctional initiator and was carried out at 70 °C for 1 h. The viscous liquid was dissolved in THF and was passed through an alumina column to remove the copper catalyst and was then dried under vacuum at 45 °C. Yield: 4.54 g (92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.9 (2H, $-OCH_2$), 2.3 (⟩CH− main chain backbone), 1.8 (1H, ⟩CH−), 1.6 (2H, ⟩CH_2- main chain backbone), 1.4 (8H, ⟩CH_2) and 0.9 ppm ($-CH_3$). $M_{n(GPC)}$ and PDI of the polymer were 1.92×10^4 g/mol and 1.15, respectively.

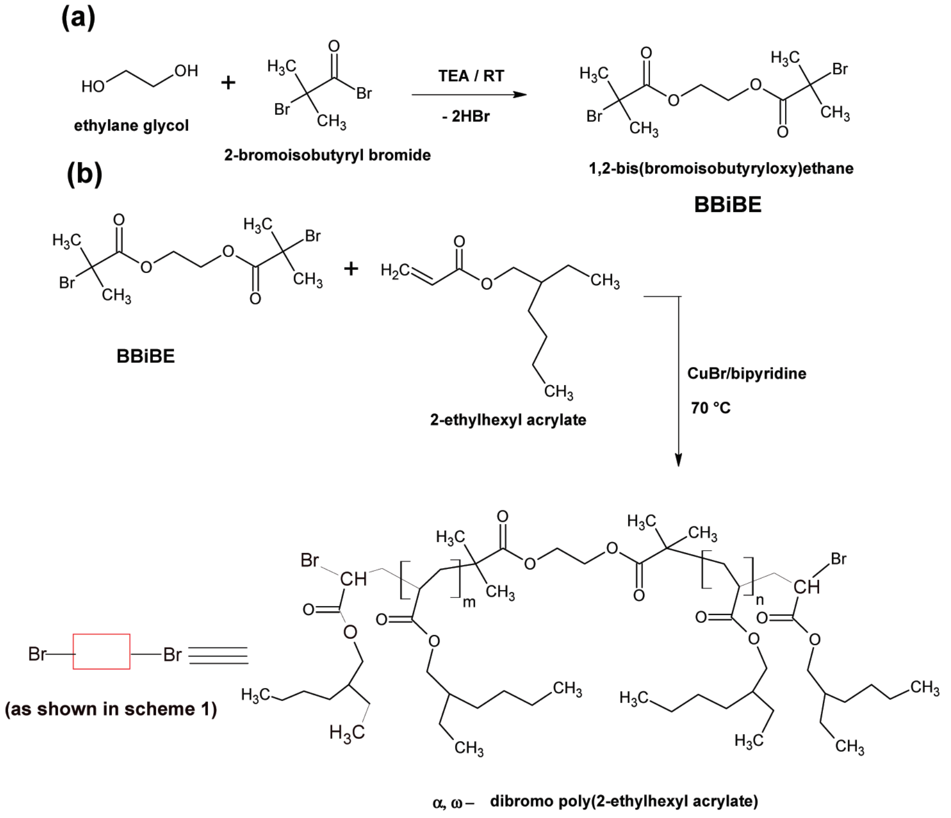
Synthesis of PFMA-b-PEHA-b-PFMA (*FEF*) *Triblock Copolymer by ATRP*. ABA triblock copolymers of different block length were prepared to use a different feed ratio of Br−PEHA−Br, the macroinitiator, and FMA, the monomer. In a typical experiment, PEHA macroinitiator (Br−PEHA−Br) [M_n = 1.92×10^4, PDI = 1.15] (2.863 g, 1.49×10^{-4} mol) was dissolved in 1 mL of dry THF and added into the round-bottom flask containing CuCl (0.015 g, 1.49×10^{-4} mol), HMTETA (0.034 g, 1.49×10^{-4} mol), and FMA monomer (3.00 g, 1.80×10^{-2} mol). The flask was sealed with silicon rubber septum, and the reaction was carried out under a nitrogen atmosphere for 1 h. The polymerization was started after addition of the initiator and was carried out at 90 °C for 30 min. The viscous liquid was dissolved in THF and was passed through an alumina column to remove the copper catalyst and was then dried under vacuum at 45 °C. The similar procedure was adopted for the polymerization of other feed ratio of the triblock copolymer. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.4 (s, 1H, =CH−O− in furan ring), 6.4 to 6.3 (m, 2H, =CH−CH= of furan ring), 4.9 (s, 2H, $-OCH_2-$ of PFMA part), 3.9 (d, 2H, $-OCH_2$ of PEHA part), 2.3 (s, ⟩CH− of PEHA unit), 1.8 (s, 1H, ⟩CH− of PEHA unit), 1.4 (s, 8H, ⟩CH_2 of PEHA unit), 1.6 and 0.9 ppm (⟩CH_2 and $-CH_3$ of main chain backbone of PFMA and PEHA units). $M_{n(GPC)}$ and PDI of the polymer were 3.74×10^4 g/mol and 1.28, respectively.

Synthesis of Thermoreversible Diels−Alder (*DA*) *Cross-Linked Polymer*. Poly(FMA-*b*-EHA-*b*-FMA) triblock copolymer (1.00 g, 2.67×10^{-5} mol) and 20 mL of dichloromethane were taken in a 100 mL round-bottom flask. The solution of 1,1-(methylenedi-4,1-phenylene)bismaleimide (BM) (1.00 g, 2.79×10^{-3} mol) was added into the round-bottom flask and stirred at room temperature, followed by heating at 120 °C under a nitrogen atmosphere for 30 min. The flask was sealed with a condenser in one neck and a silicon rubber septum in the other. The reaction mixture was kept at room temperature for 24 h, and the cross-linked polymer was obtained. The final product was dried in a vacuum oven for 12 h. Yield: 1.60 g (80%). FT-IR (KBr): 3133 (C−H stretching of aromatic ring), 2958 (C−H stretching), 1711 (⟩CO), 1638 (⟩C=C⟨), 1395 (−C−N−C−), 827 cm^{-1} (benzene ring in the maleimide unit).

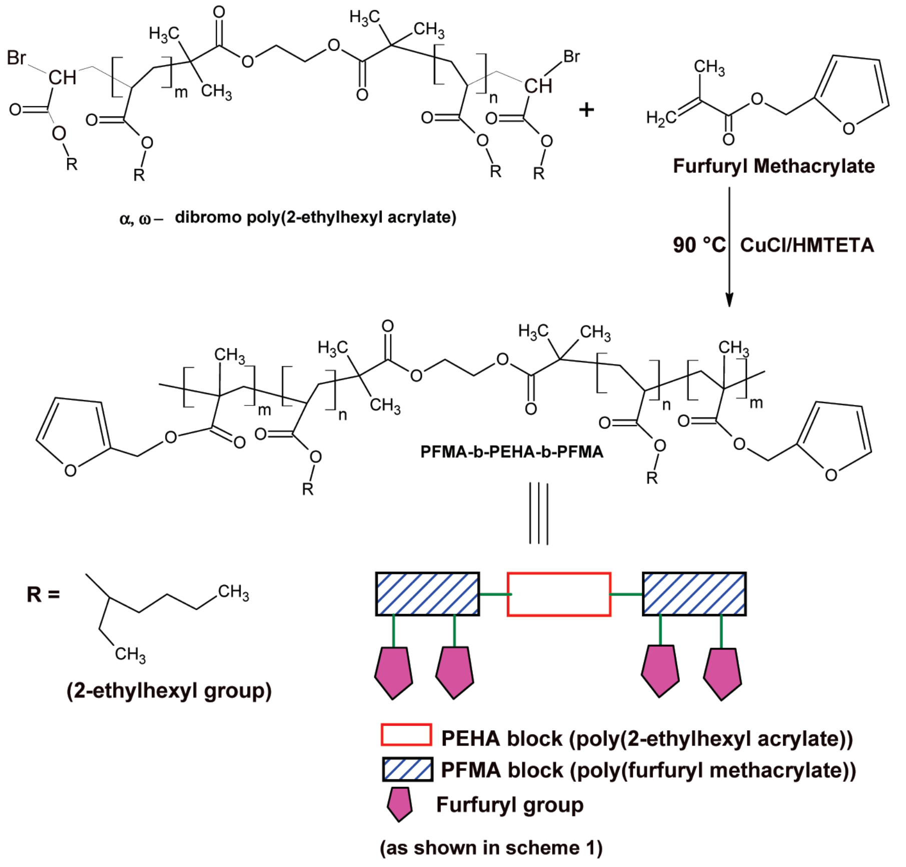
Results and Discussion

Synthesis and Characterization of ABA Triblock Copolymer. The triblock copolymer PFMA-*b*-PEHA-*b*-PFMA (FEF) was synthesized via ATRP at 90 °C using CuCl/HMTETA as the catalyst. The synthesis was carried out in two steps, as shown in Schemes 2 and 3. The difunctional

Scheme 2. (a) Synthesis of Difunctional Initiator; (b) ATRP of 2-Ethylhexyl Acrylate (EHA) To Prepare Difunctional Macroinitiator



Scheme 3. Synthesis of ABA (Poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-(polyfurfuryl methacrylate) [PFMA-*b*-PEHA-*b*-PFMA]) Triblock Copolymer



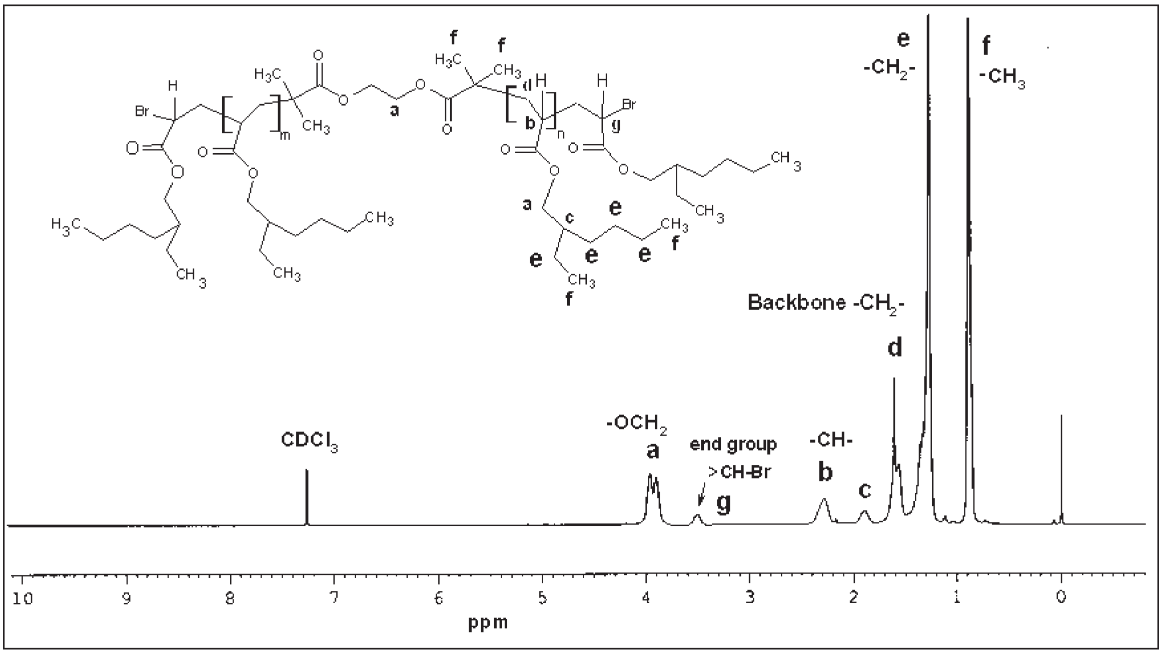


Figure 1. ^{1}H NMR spectra of α,ω-dibromo-poly(2-ethylhexyl acrylate) (Br−PEHA−Br) macroinitiator.

Table 1. Characterization of Poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF) Triblock Copolymers via ATRP of Furfuryl Methacrylate Using PEHA as ATRP Macroinitiator

								final composition (NMR)	
no.	polymer	feed composition EHA/FMA/EHA	DP (final polymer)	conversion (%)	$M_{n(GPC)}$ (g/mol)	$M_{n(theo)}$ (g/mol)	PDI	$M_{n(NMR)}$	PFMA (hard segment) (%)
1	PEHA (macroinitiator)		$EHA_{(104)}$	92	1.92×10^4	1.84×10^4	1.15	18 580	
2	FEF-1	5−20−5	$FMA_{(26)}$:$EHA_{(104)}$:$FMA_{(26)}$	88	2.77×10^4	$2.78 \times 10^{4\,a}$	1.31	27 330	32
3	FEF-2	10−20−10	$FMA_{(55)}$:$EHA_{(104)}$:$FMA_{(55)}$	93	3.74×10^4	$3.78 \times 10^{4\,a}$	1.28	36 420	49
4	FEF-3	20−20−20	$FMA_{(102)}$:$EHA_{(104)}$:$FMA_{(102)}$	89	5.29×10^4	$5.48 \times 10^{4\,a}$	1.30	51 620	64

[a] These $M_{n(theo)}$ values were calculated using $M_{n(GPC)}$ of 1.92×10^4 of PEHA block (no. 1).

initiator [1,2-bis(bromoisobutyryloxy)ethane] (BBiBE) was synthesized by the esterification reaction between ethylene glycol and 2-bromoisobutyryl bromide as shown in Scheme 2a. Using this difunctional initiator, α,ω-dibromo-PEHA was synthesized by the ATRP route using CuBr/bipyridine as the catalyst system (Scheme 2b). The macroinitiator (α,ω-dibromo-PEHA) had the M_n and polydispersity index values 19 220 and 1.15, respectively. Figure 1 shows the ^{1}HNMR of α,ω-dibromo-PEHA (macroinitiator). The characteristic resonances at δ = 3.9, 2.3, 1.8, 1.6, 1.4, and 0.9 ppm are due to the $-OCH_2$ (designated as "a"), ⟩CH− (main chain backbone, designated as "b"), ⟩CH− (side chain, "designated as c"), ⟩CH_2 (main chain backbone, designated as "d"), ⟩CH_2 (side chain, designated as "e"), and $-CH_3$ (designated as "f") protons, respectively. The small resonance at 3.6 ppm are due to the ⟩CH−Br end group of the polymer. The $M_{n(NMR)}$ of the macroinitiator was calculated by using end-group analysis from the ^{1}H NMR spectra. The details and the characterization data are given in Table 1. The M_n values of the macroinitiator and those of the triblock copolymers are also calculated by GPC analysis (Table 1).

The above-mentioned macroinitiator (α,ω-dibromo-PEHA) was used to prepare a series of the FMA-*b*-PEHA-*b*-PFMA (FEF) triblock copolymers with varying composition as shown in Table 1. The second block was prepared by polymerization of the second monomer FMA by using different monomer to macroinitiator ratio (Table 1). Scheme 3 shows the synthesis of FEF triblock copolymer via ATRP. The block copolymer was purified by passing through an alumina column and then was precipitated from *n*-hexane, which is a nonsolvent for both the blocks. Figure 2 shows the GPC traces of the PEHA macroinitiator (M_n = 1.92 × 10^4 g/mol) and the triblock copolymer (M_n = 3.74 × 10^4 g/mol). The complete shift of the GPC traces toward higher M_n maintaining low polydispersity index indicates successful block copolymerization and good initiator efficiency of Br-PEHA-Br for FMA.

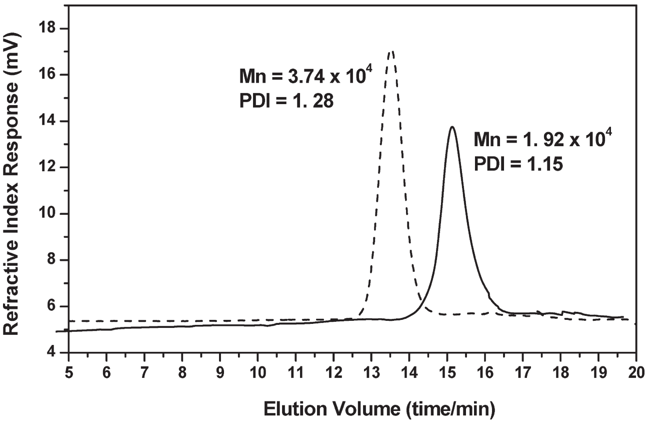


Figure 2. GPC traces of the Br−PEHA−Br macroinitiator and the block copolymers.

The block copolymers FEF-1, FEF-2, and FEF-3 indicate the different block length of the hard−soft−hard segment of

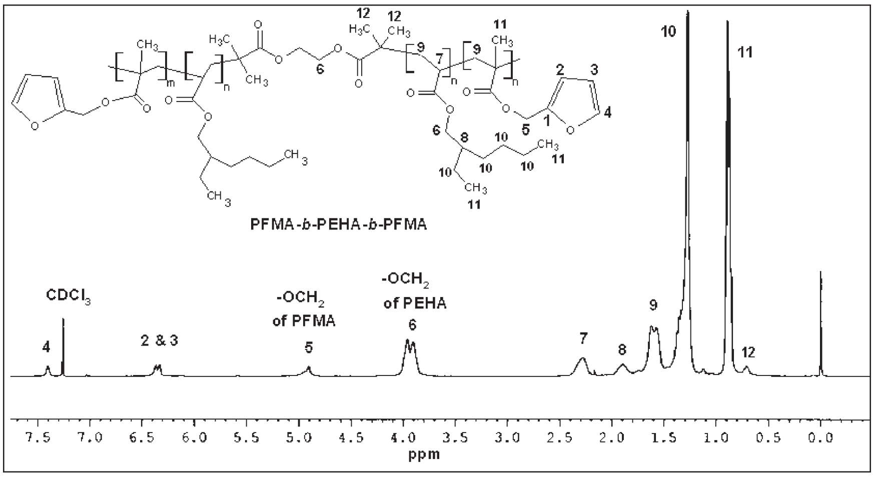


Figure 3. ^{1}H NMR spectra of poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) triblock copolymer.

5–20–5 (5000–20000–5000), 10–20–10, and 20–20–20, respectively. The final composition and the incorporation of FMA were confirmed by ^{1}H NMR spectroscopy. Figure 3 shows the ^{1}H NMR spectra of the PFMA-*b*-PEHA-*b*-PFMA triblock copolymer of FEF-1. The composition of the block copolymers was determined from integral area of the resonances of $-OCH_2$ protons ($\delta = 5.0$ ppm) in the PFMA blocks (designated as "5" in Figure 3) and that of $-OCH_2-$ protons ($\delta = 4.0$ ppm) in the PEHA blocks (designated as "6" in Figure 3). The compositions of the block copolymers as well as their molecular weights calculated from ^{1}H NMR spectra had a good agreement with those determined by GPC analysis (Table 1).

Controlled polymerization and incorporation of FMA into the copolymer is very challenging because of the side reaction involving the reactive functionality.[8,31] Conventional radical polymerization of FMA leads to gel formation due to the excessive chain transfer involving the C_4 proton (designated as "4") and $-OCH_2$ protons (designated as "5") in FMA (Figure 3).[8] In this investigation we have successfully prepared FEF triblock copolymers with controlled molecular weight without any gel formation. The resultant block copolymer was soluble in many organic solvents. The polymers were dissolved in THF and were film cast to study their mechanical properties.

Thermal and Mechanical Studies of ABA Triblock Copolymer. *DSC.* DSC analysis showed that FEF triblock copolymer (PFMA-*b*-PEHA-*b*-PFMA) has two T_gs (Figure 4). The T_gs of the polymers are shown in Table 2. T_g for the PFMA homopolymer was +64 °C,[9] and that for the homopolymer PEHA was −58 °C.[32] In the case of FEF-2 block copolymer we observed two T_gs: one of hard segment at +65 °C (PFMA) and another of soft segment at −50 °C (PEHA). Also, it is found that with increase in hard segment content T_g of the block copolymer slightly increases. The increase in T_g for the different blocks in the block copolymers, especially for the soft phase, is due to the restriction in the free chain mobility of the polymer molecules.

Tensile Properties. Figure 5 depicts the stress–strain plots for FEF triblock copolymers having varying length of hard segment. FEF-1, FEF-2, and FEF-3 represent the triblock copolymers having various length of hard–soft–hard segment of 5–20–5, 10–20–10, and 20–20–20, respectively. The increase in final polymer molecular weight has a direct relationship with the chain length of hard segments, as the length of soft segment is fixed at 20 000. Table 3 shows the tensile properties of the triblock copolymers having varying lengths of hard segment.

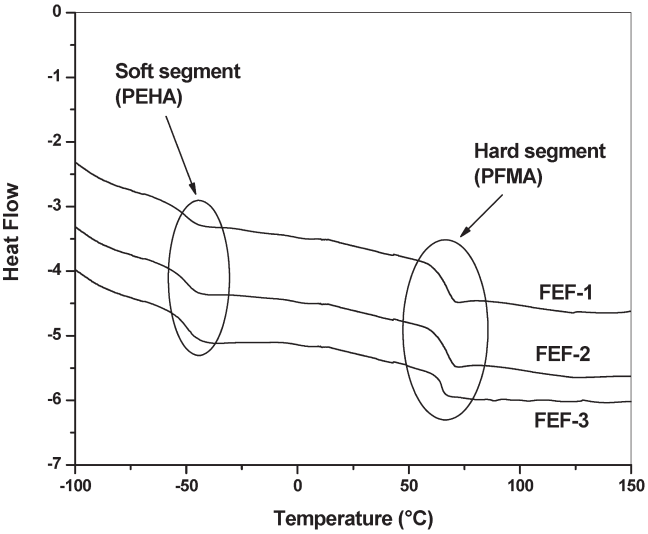


Figure 4. Differential scanning calorimetry (DSC) thermograph of poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF) triblock copolymer.

Table 2. Glass Transition Temperature (T_g) of the Poly(furfuryl methacrylate)-*b*-poly(2 ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF) Triblock Copolymers

		DSC		DMA	
polymer	feed composition	T_g I (°C)	T_g II (°C)	T_g I (°C)	T_g II (°C)
FEF-1	5–20–5	−52	+63	−35	+88
FEF-2	10–20–10	−50	+65	−33	+90
FEF-3	20–20–20	−46	+67	−30	+92

The stress–strain plot (Figure 5) for FEF-1 resembles that of a nonstress crystallizing elastomer. The strain shows very high value even at low stresses. The ultimate tensile strength and elongation at break for FEF-1 triblock copolymer are 3.0 MPa and 42.8%, respectively, which are in the range of that of an unfilled synthetic elastomer. The tensile modulus value of 8.2 MPa shows less resistance to flow when an external force is applied to it. This is an indicative of the prominence of elstomeric PEHA block present in the block copolymer, which takes the majority of the applied stress and deforms into high elongations. On the other hand, the stress–strain plot for FEF-2, which has equal block lengths of both elastomeric PEHA and thermoplastic PFMA domains, shows a ductile failure under elongation. This behavior is a common feature of thermoplastic elastomers, which has a moderate tensile strength of 14.2 MPa, but shows a yield before the actual failure at 20.2% strain. The initial high modulus (114.4 MPa) corresponds to the plastic blocks which restricts the flow up to a critical stress level. The yielding is a feature of the elastomeric part which is attributed to the uncoiling and chain slippage in between the elastomeric chains. FEF-3 shows a completely brittle fracture and shows no yielding during its tensile property measurements. It has a very high ultimate tensile strength value of 35.4 MPa and a very low elongation at break of 15.9%. This underlines the dominance of rigid PFMA blocks that takes most of the loads and the minor elastomeric parts has no role in strengthening the copolymer.

Tension set values of FEF-1, FEF-2, and FEF-3 are 4.8%, 36.8%, and 64.0%, respectively. FEF-1, which has more elastomeric block length, shows the lowest set value and thereby maximum set property. This is attributed to the dominance of elastomeric blocks which has a tendency to retract completely to the initial length upon the removal of a deforming force. FEF-2, on the other hand, shows considerable set but not as much as FEF-3. The set value for FEF-2 is well under that required for thermoplastic elastomers, for which the maximum specified set value is 50%.[33] FEF-3 behaves similarly to a thermoplastic and shows a higher set value of 64%, indicating poor set property.

Dynamic Mechanical Properties: Effect of Temperature. The temperature dependence of the storage modulus (G') and tan δ for three FEF triblock copolymers are shown in Figure 6a,b. Figure 6a depicts the variation of storage modulus of the copolymers with temperature. The FEF block copolymer having larger PFMA block (FEF-3) shows higher storage modulus followed by FEF-2 with equal block lengths of PFMA and PEHA. The lowest value is shown by the block copolymer having longer PEHA block and lowest content of PFMA (FEF-1). During transition, the storage modulus exhibits a sharp dip, and the temperature corresponds to the glass transition temperature (T_g) of the triblock copolymers. Figure 6b (tan δ vs temperature) shows two glass transitions and an intermediate rubbery region for all the block copolymers. T_g can be easily located using tan δ vs temperature curve shown in Figure 6b. It clearly shows two distinct T_gs for two blocks in the copolymers (Table 2). It can be mentioned that the T_g obtained by DMA analysis was higher than those obtained by DSC analysis (Table 2). In fact, the T_g value of a particular polymer varies with the type of measuring technique. These methods monitor certain physical parameters with function of temperature. The T_g is a temperature at which there is a sharp change in the observed parameter. DSC analysis uses specific heat capacity while DMA observes the change in modulus of the material at the T_g range. In dynamic mechanical analysis, the sample is subjected to cyclic loading, and thereby the chains become flexible at relatively higher temperatures as compared to the DSC method, which observes the temperature at which molecular chain mobility suddenly starts. Figure 6b also indicates that the nature of tan δ curve is controlled by the block lengths in the block copolymers. The height of the damping factor (tan δ) peak corresponds to length of the respective blocks. The temperature sweep for FEF-2 has two tan δ peaks of almost equal height. In this block copolymer the hard and soft block contents are almost equal. Tan δ curves for the block copolymers that have preferably one segment in excess, its tan δ peak is dominated over the other segment. Thus, the dynamic mechanical study using temperature sweep provides information about the existence of two blocks and its relative quantity in the copolymer.

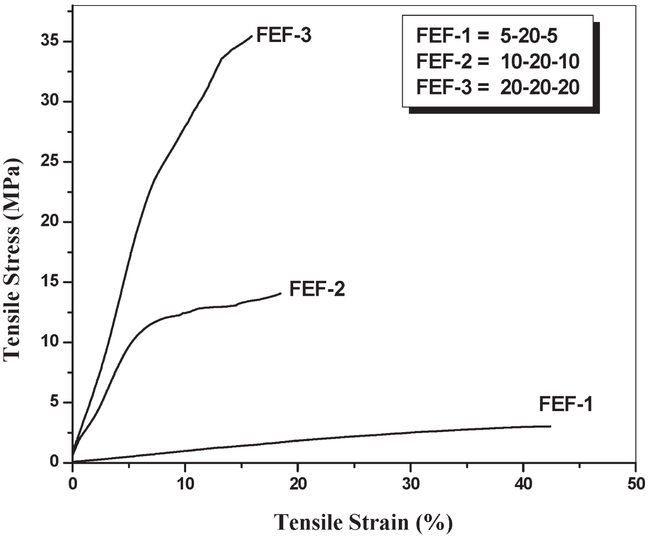


Figure 5. Stress−strain curves for poly(furfuryl methacrylate)-*b*-poly-(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF) triblock copolymers.

Thermoreversible ABA Triblock Polymer for Self-Healing Application via Diels−Alder Reaction. Different polymers are being used in self-healing materials that have different potential applications.[34−36] Reversible features of Diels−Alder (DA) and retro-Diels−Alder (rDA) can be used to prepare self-healing polymeric materials. DA reaction generally provides simple and efficient methods to generate new bonds by inter- or intramolecular [4 + 2] cycloaddition between diene and dienophiles. One of the interesting features of this reaction is that it is thermally reversible. This implies that its equilibrium can be easily displaced toward the reagents by heating (rDA).[8] In the present case the DA reaction was carried out between PFMA-*b*-PEHA-*b*-PFMA (FEF-2) and 1,1-(methylenedi-4,1-phenylene)bismaleimide (BM) as shown in Scheme 4. Equal quantities of FEF-2 and BM (1:1, by mole) were dissolved in dichloromethane and stirred at room temperature followed by heating at 120 °C for 1 h under a nitrogen atmosphere. Then the reaction mixture was kept under room temperature for 24 h, and the cross-linked DA polymer was obtained. The thermoreversible DA polymer was characterized by FTIR, DSC (by heating and cooling cycle), and SEM analysis. Figure 7 shows the FTIR spectra of the FEF-2 triblock copolymer, FEF-2, and BM mixture at $t = 0, 4, 12,$ and 24 h. Figure 7a shows that FEF-2 triblock copolymer has intense peaks at 1012 and 1153 cm^{-1} which are attributed due to the ring

Table 3. Tensile Properties of Different Poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF) Triblock Copolymers

polymer	different block length (PFMA−PEHA−PFMA)	$M_{n(GPC)}$ (g/mol)	Young's modulus (MPa)	ultimate tensile strength (MPa)	elongation at break (%)	tension set (%)
FEF-1	5−20−5	2.77×10^4	8.2	3.0	42.8	4.8
FEF-2	10−20−10	3.74×10^4	114.4	14.2	20.2	36.8
FEF-3	20−20−20	5.29×10^4	265.7	35.4	15.9	64.0

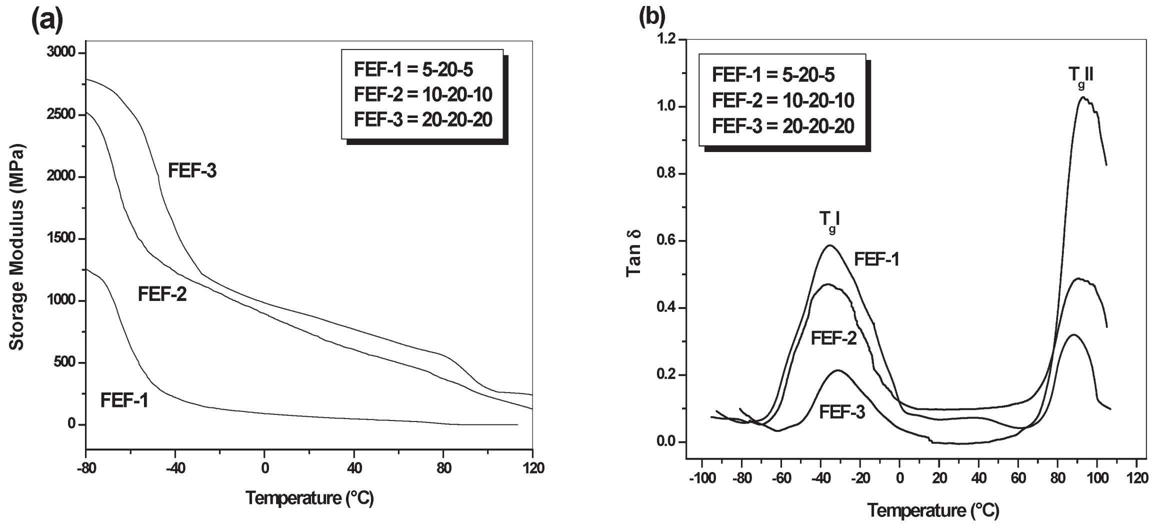
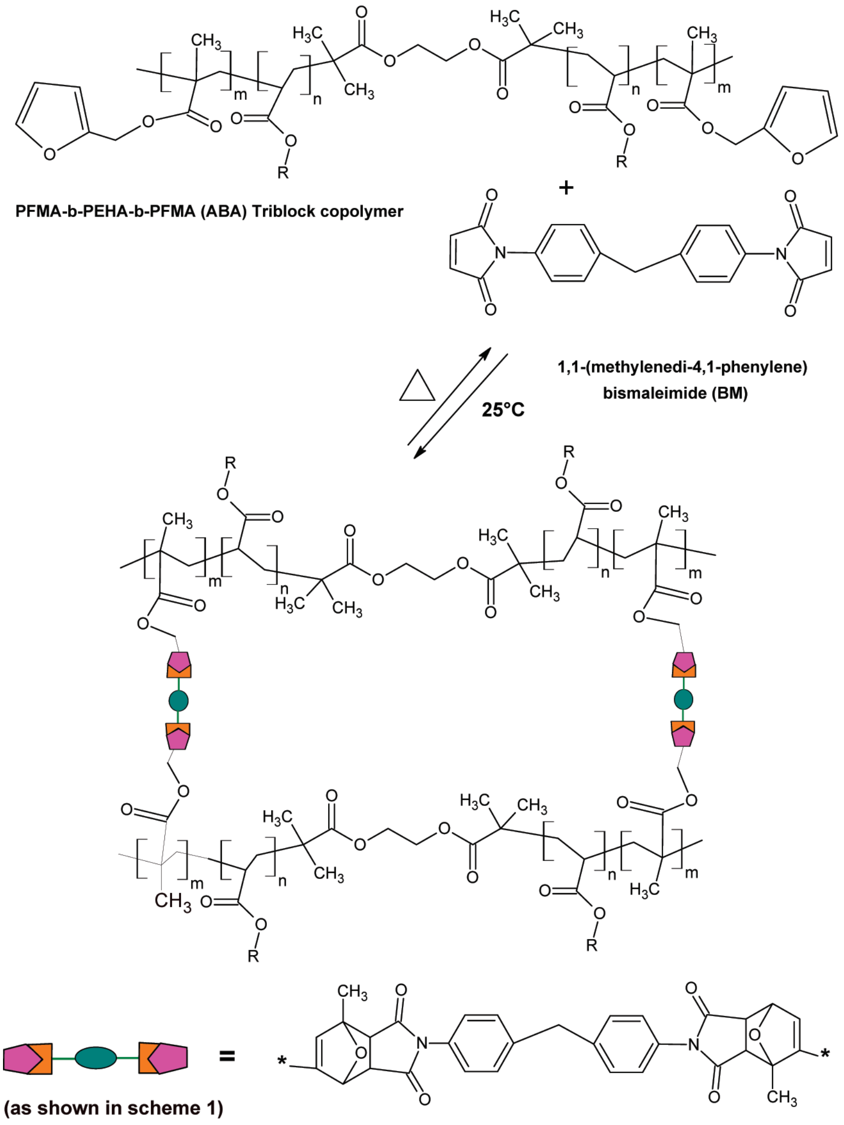


Figure 6. Dynamic mechanical analysis (DMA) of the poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF) triblock copolymers: (a) storage modulus; (b) tan δ.

Scheme 4. Synthesis of Diels−Alder (DA) Cross-Linked Smart Polymer



breathing and ether linkage in the furfuryl ring, respectively. Figure 7b shows the mixture of FEF-2 and BM at t = 0 h. The peak at 1395 cm^{-1} due to the −C−N−C− of maleimide and the characteristic peaks (i.e., peaks at 1012 and 1153 cm^{-1}) for the furfuryl groups are in the same position and are not affected at t = 0 h. Parts c, d, and e of Figure 7 show the reaction between FEF-2 and BM at t = 4, 12, and 24 h, respectively. Figure 7c,d shows the disappearance of peak at 1012 cm^{-1} and the formation of new peak at 1636 cm^{-1}, which indicates the formation of ⟩C═C⟨ due to the DA cross-link between FEF-2 triblock copolymer and BM. The shifting of ⟩C═O peak from 1727 to 1711 cm^{-1} is due to the interaction between PFMA and BM.[37]

Thermoreversible Studies of the Self-Healing Triblock Copolymer. *DSC Studies.* Thermoreversible study was further confirmed by DSC analysis. Figure 8 shows the heating and cooling curves of DSC analysis of the FEF-2-BM and DA cross-linked polymer. Figure 8a shows the first heating curve of the cross-linked polymer heated at −100 to 200 °C. The curve "A" shows the first heating cycle. It has an endothermic peak at 150 °C, which indicated the cleavage of the DA cross-links. The curve "B" shows the cooling curve of the polymer. It shows a broad exothermic peak at 122−180 °C due to the covalent bond formation between furan and maleimide moieties, as the samples come closer on cooling and then finally reconnect very efficiently. The curve "C" shows the second heating cycle of the DA cross-linked polymer. It also shows the same observation in the first heating cycle. It clearly indicates that the Diels−Alder cross-linked block polymer (FEF-2-BM) is thermoreversible. The $T_{\rm g}$s of the polymer were determined from the second heating cycle of the polymers and are shown in Figure 8b. The transition at 114 °C is due to the $T_{\rm g}$ of the hard segment (PFMA-BM). The shifting of hard segment $T_{\rm g}$ from +65 to 114 °C is due to the DA cross-linked between PFMA and BM. The transition at −44 °C (Figure 8b) is due to the $T_{\rm g}$ of (PEHA) the soft segment. The shifting of $T_{\rm g}$ from −50 to −44 °C is due to the restriction of the chain mobility in DA cross-links.

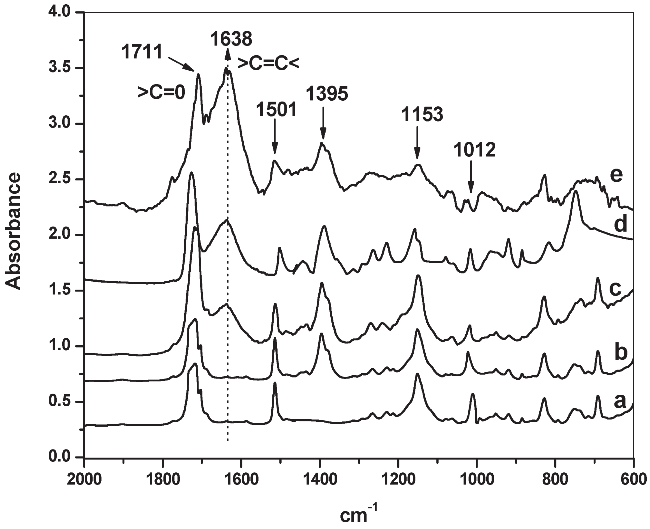


Figure 7. FTIR spectra of the DA polymer: (a) poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF-2); (b) FEF-2 + BM at t = 0; (c, d, e) FEF-2 + BM at t = 4, 12, and 24 h, respectively.

SEM Studies of the Self-Healing Cross-Linked Smart Polymer. The self-healing behavior of the thermoplastic FEF-2-BM triblock DA cross-linked films was characterized by SEM studies (Figure 9). The cross-linked materials show very smooth planar surface as shown in Figure 9a. A deliberate scratch was made on the FEF-2-BM film surface using a knife (Figure 9b). The knife-cut sample was thermally heated at 120 °C for 4 h and kept at 25 °C for 24 h. At a different time interval the samples were characterized by SEM analysis. Parts c−f of Figure 9 show the FEF-2-BM samples heated at 120 °C at different time intervals of 1, 2, 3, and 4 h, respectively. It shows that the cleavage of the covalent bonds occurs slowly due to rDA in the cross-linked polymer. Since the cleavage of bonds between furfuryl group and BM, the polymeric materials slowly get enhanced mobility and bonded again via DA reaction as shown in Figure 9c−e. Finally Figure 9f shows that the polymer self-heals to show a complete notch recovery to regain its earlier structure (Figure 9a).

Solution Properties of the Cross-Linked Smart Polymer. The solution properties of the thermoreversible cross-linked DA polymer (FEF-2-BM) were studied using toluene as solvent at 25 and 100 °C. Scheme 5 shows the general schematic representation of the solution behavior of the FEF-2-BM cross-linked polymer. The solid FEF-2-BM polymer (polymer a) was taken in a 25 mL round-bottomed flask followed by the addition of toluene at 25 °C (sample b).

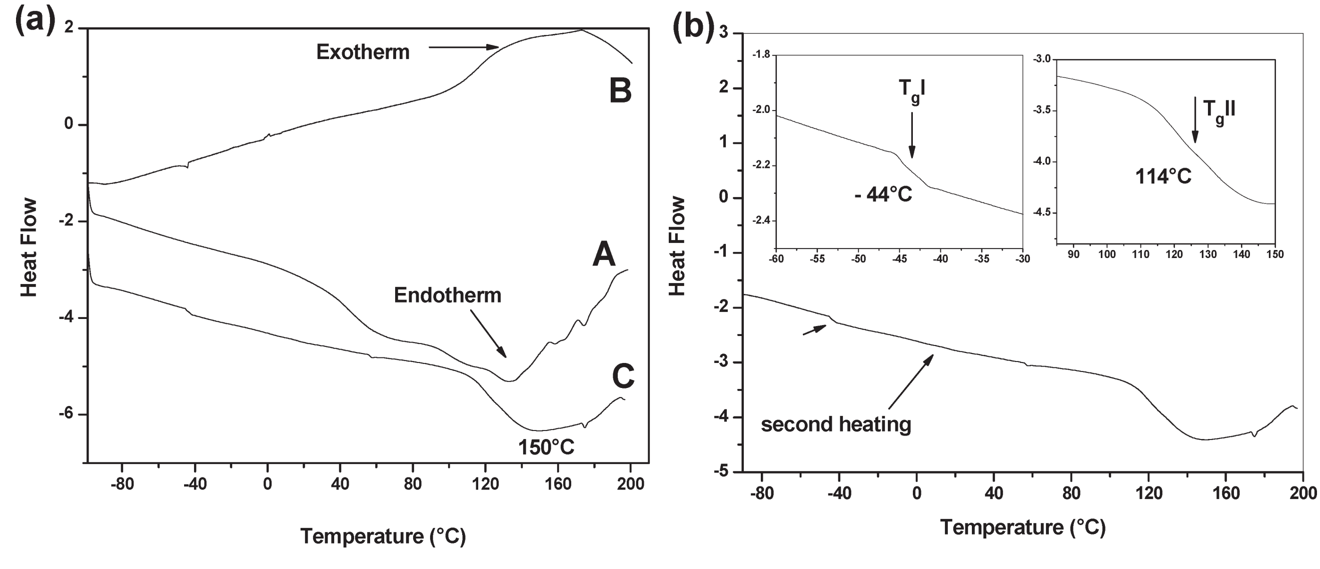


Figure 8. DSC analysis of the polymer. (a) DSC curve for the cross-linked polymer poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate)-2-bismaleimide (FEF-2-BM): (A) first heating curve, (B) cooling curve, and (C) second heating curve. (b) $T_{\rm g}$ of the cross-linked polymer.

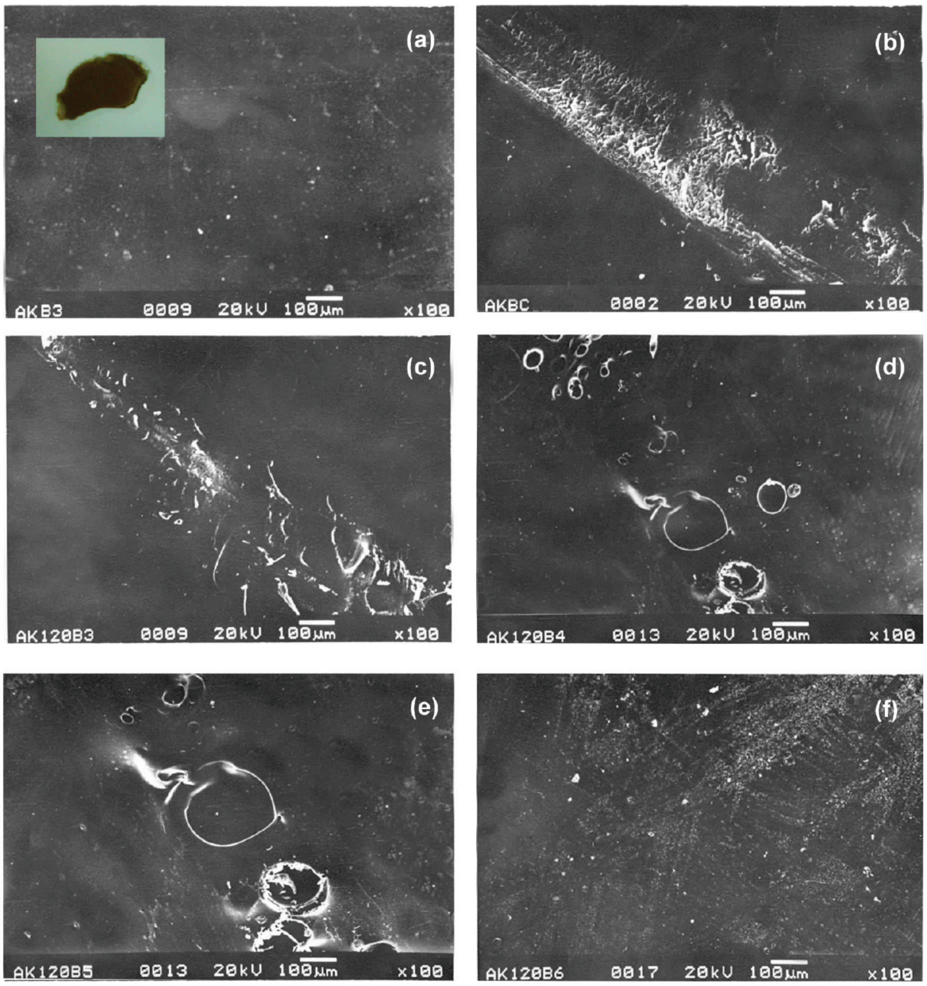


Figure 9. Self-healing study of poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate)-2-bismaleimide (FEF-2-BM) triblock DA cross-linked polymer. SEM images of (a) cross-linked polymer and (b) knife-cut sample. (c, d, e, f) Heating of FEF-2-BM triblock DA cross-linked polymer at different times of 1, 2, 3, and 4 h, respectively.

It was closed and kept at room temperature for 2 h. It was observed that the cross-linked polymer was insoluble at 25 °C (sample c) and got swollen, indicating the cross-linking reaction between FEF-2 and BM. When it was heated at 100 °C for 9 h, it becomes soluble (Scheme 5d). It indicates the retro-DA (rDA) reaction which led to the cleavage of furfuryl ring (in the FEF triblock copolymer) and bismaleimide. This rDA was also confirmed by FTIR analysis. Figure 10 shows the FTIR spectra of the sample "d" (in Scheme 5). It shows the disappearance of the $\rangle C{=}C\langle$ peak at 1636 cm^{-1} and the emergence of new peaks at 1501 and 1395 cm^{-1} which are attributed to the furan ring stretching and $-C-N-C-$ of bismaleimide, respectively. It indicates the clear evidence of rDA reaction. The soluble polymer (sample d in Scheme 5) was kept at 25 °C for 2 days. The solvent was evaporated slowly from the solution. The resultant solid FEF-2-BM adducts was cross-linked again (sample e). This reformed DA polymer was further confirmed by FTIR analysis. The FTIR spectrum of sample "e" is shown in Figure 10. It shows the emergence of the peak at 1636 cm^{-1} attributed to the formation of the $\rangle C{=}C\langle$ peak which is due to the re-formation of DA cross-linked polymer. Further addition of toluene into the re-formed DA polymer (sample e) at 25 °C had shown no solubility (sample b). Repetition of this cycle supports the thermoreversibility of the DA adduct of ABA triblock copolymer and BM.

Dynamic Mechanical Studies of Thermoreversible Self-Healing Triblock Copolymer: Effect of Frequency. Figure 11a shows the variation in storage modulus of FEF-2-BM, the DA cross-linked polymer with frequency of oscillation. The test was carried out at different temperatures ±40 °C around temperature of the thermoreversible cross-link formation. As the frequency increases, the storage modulus of the samples increases irrespective of the temperatures being used for testing. This behavior can be explained on the basis of the time-dependent molecular relaxations of polymers. As sinusoidal stress is applied at lower frequencies, polymer molecules get enough time to relax or rearrange according to the applied stress. The polymer behaves like a low viscous fluid that easily flows with an applied stress. When the frequency increases, the stress applied on the polymeric chains is too fast to have molecular rearrangements or relaxations. Hence, polymer flow gets restricted, and it behaves like a solid material. The increased storage modulus or stiffness at higher frequency is an outcome of the decreased molecular relaxations. There is decrease in storage modulus with increase in test temperature. As the temperature increases, the free volume within the polymeric material increases. This is due to the scission of thermoreversible cross-links on the DA polymer promoting more flow. The reduced stiffness (storage modulus) at higher temperature is an outcome of the cross-link scission that results in more free volume for deformations within the polymer. The sample tested at 160 °C has no considerable increase in storage modulus with increase in frequency. This can be attributed to the complete breakdown of thermoreversible bonds at 160 °C.

Figure 11b shows the variation of loss modulus with increase in frequency tested at different temperatures. The loss modulus has a direct relationship with frequency and the trend is similar to that of storage modulus with frequency. The lower loss modulus values at lower frequencies are attributed to the promoted flow and significant molecular relaxations. As the frequency increases, the loss modulus increases which is attributed to the restricted flow behavior due to the reduction in the time available for molecular relaxations. The molecular relaxations are also a function of temperature. The temperature range (80−160 °C) selected for the test contains the temperature for cleavage of cross-links in the DA polymer. Above this temperature polymeric chains are free for intermolecular slippage which causes flow. This is the reason for the lower loss modulus values at higher test temperatures.

Figure 11c demonstrates the effect of frequency on damping factor (tan δ) at different temperatures ranging from 80 to 160 °C. At lower frequencies, a higher value of tan δ corresponds to linear chain and a low value indicates branching or cross-linking in the polymers.[38] The samples tested at 160 °C gave the highest damping factor at lower frequency as compared to its lower temperature scans. It indicates that the DA cross-links break down at higher temperatures, giving a relatively linear structure. Also, the peak height of damping factor decreases with decrease in temperature. At higher temperatures more damping is expected because of the scission of cross-links. However, at higher frequencies higher tan δ values are obtained for samples tested at lower temperatures. This may be attributed to the increased effective molecular weight of the cross-linked polymers at lower temperatures which shows higher damping as compared to easily flowable linear chains that deforms easily at higher frequencies. This study also draws conclusions that the DA cross-links break at higher temperatures, transforming the cross-linked structure to a more linear structure.

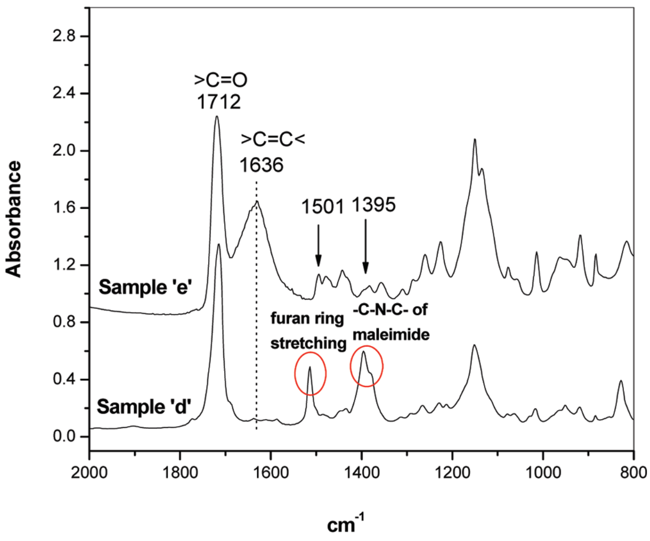
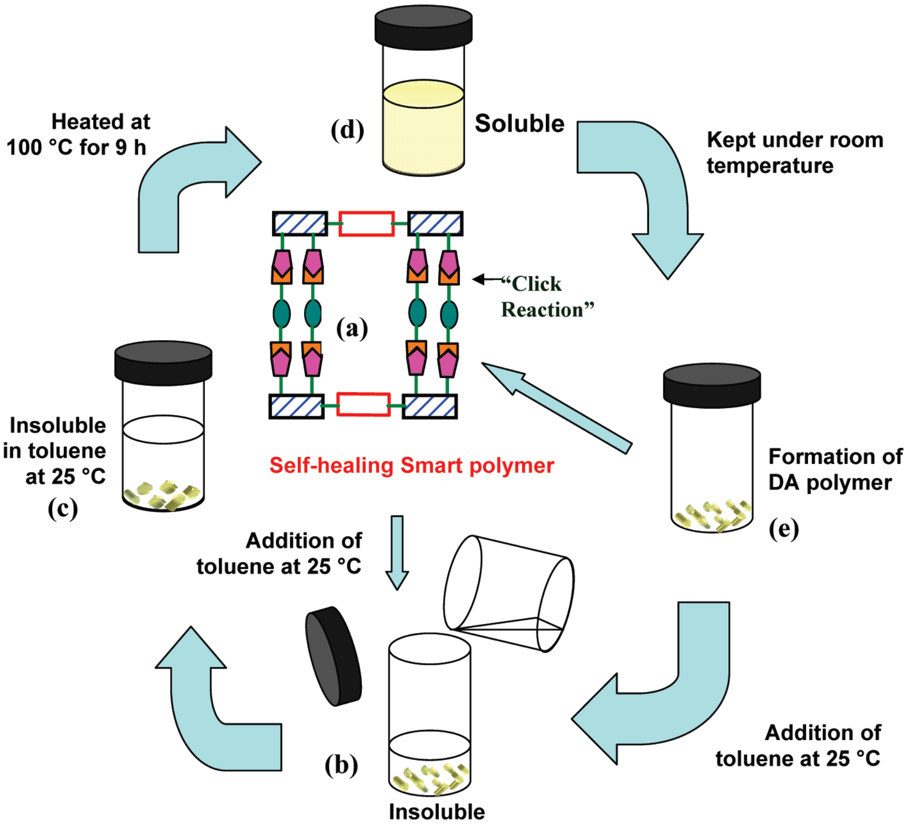


Figure 10. FTIR spectra of sample “d” and sample “e” (as shown in Scheme 5).

Scheme 5. General Schematic Representation of the Solution Behavior of the Poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate)-2-bismaleimide (FEF-2-BM) Cross-Linked Polymer: (a) FEF-2-BM Cross-Linked Polymer, (b) Addition of Toluene at 25 °C; (c) Insoluble Cross-Linked Polymer at 25 °C for 2 h; (d) Soluble FEF-2-BM Cross-Linked Polymer at 100 °C for 9 h; and (e) Soluble FEF-2-BM Polymer Cross-Linked Again at 25 °C after 2 days



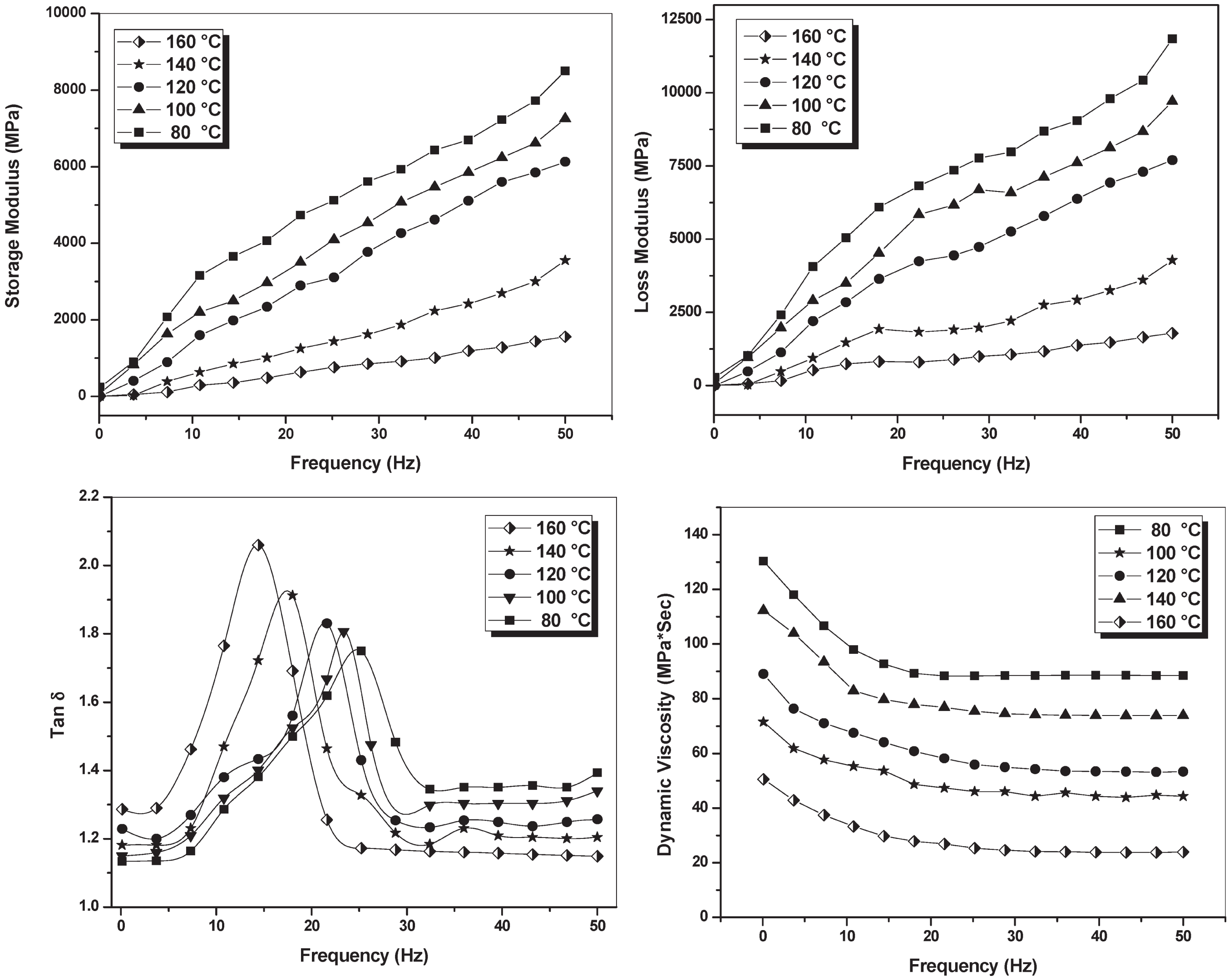


Figure 11. Frequency sweep dynamic mechanical spectra of poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate)-2-bismaleimide (FEF-2-BM) polymer: (a) storage modulus, (b) loss modulus, (c) damping factor (tan δ), and (d) dynamic viscosity.

Figure 11d shows the variation of complex viscosity (η') with frequency. The dynamic viscosity was calculated from eq 1.

$$\eta' = \frac{E''}{\omega} \tag{1}$$

where E'' is the loss modulus and ω the frequency.[39]

As the frequency of the test increases, the complex viscosity of samples was found to be decreasing. This observation is similar to the "shear thinning" effect of polymeric material with increase in shear rate in classical rheological tests. The viscosity values at higher temperatures were significantly lower than those at lower temperatures. This is attributed to the thermal cleavage of DA cross-links in the polymeric material which causes easy molecular slippage between the chains. This study supports the facts that the DA cross-links break at higher temperatures and reform again at lower temperature range.

Conclusions

A series of ABA triblock copolymer [(poly(furfuryl methacrylate)-*b*-poly(2-ethylhexyl acrylate)-*b*-poly(furfuryl methacrylate) (FEF)] bearing a reactive pendant furfuryl group was successfully prepared by atom transfer radical polymerization. Molecular weights and chemical composition of the polymers are determined by gel permeation chromatography and ^{1}H NMR. Differential scanning calorimetric (DSC) analysis showed two T_gs: one for the soft segment of PEHA block and another for the hard segment of PFMA block. Thermoreversible smart polymers were prepared successfully by using the "click chemistry" of the Diels–Alder (DA) reaction between the furfuryl group of FEF triblock copolymer as diene and bismaleimide (BM) as the dienophile. The self-healing nature of the FEF-BM polymer was studied by SEM analysis, and the complete healing was observed in 4 h. Interestingly, the thermoreversible nature of the DA polymer was characterized by DSC, solution, dynamic mechanical analysis, and FTIR analysis. This example of "click chemistry" in tailor-made reactive triblock thermoplastic elastomeric block copolymer can have interesting applications, like in thermoreversible smart materials, self-repairing coating and adhesives, and biomaterials.

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References and Notes

(1) Wu, D. Y.; Meure, S.; Solomon, D. *Prog. Polym. Sci.* **2008**, *33*, 479–522.

(2) (a) Dry, C. M. *J. Intell. Mater. Syst. Struct.* **1993**, 420–4255. (b) Dry, C. M.; Sottos, N. R. *Technomic* **1992**, 438−44.

(3) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R. *Nature* **2001**, *409*, 794–797.

(4) Schmets, A. J. M.; Zwaag, V. S. Proceedings of the first international conference on self healing materials. In *Supplement to Springer Series in Materials Science*; Springer: Noordwijk, Netherlands, 2007; Vol. *100*.

(5) Carlson, H. C.; Goretta, K. C. *Mater. Sci. Eng., B* **2006**, *132*, 2–7.

(6) Jud, K.; Kausch, H. H.; Williams, J. G. *J. Mater. Sci.* **1981**, *16*, 204–210.

(7) (a) Yamaguchi, M.; Ono, S.; Terano, M. *Mater. Lett.* **2007**, *61*, 1396–1399. (b) Gupta, S.; Zhang, Q.; Emrick, T.; Balazs, A. C.; Russell, T. P. *Nat. Mater.* **2006**, *5*, 229–233.

(8) Gheneim, R.; Perez-Berumen, C.; Gandini, A. *Macromolecules* **2002**, *35*, 7246–7253.

(9) Goiti, E.; Huglin, M. B.; Rego, J. M. *Polymer* **2001**, *42*, 10187–10193.

(10) (a) Goiti, E.; Heatley, F.; Huglin, M. B.; Rego, J. M. *Eur. Polym. J.* **2004**, *40*, 1451–1460. (b) Kavitha, A. A.; Singha, N. K. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1427–1436.

(11) Davidenko, N.; Zaldivar, D.; Peniche, C.; Sastre, R.; Roman, J. S. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2759–2766.

(12) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.

(13) (a) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Frechet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928–3932. (b) Golas, P. L.; Matyjaszewski, K. *Comb. Sci.* **2007**, *26*, 1116–1134. (c) Deng, G.; Ma, D.; Xu, Z. *Eur. Polym. J.* **2007**, *43*, 1179–1187.

(14) Kyeremateng, S. O.; Amado, E.; Blume, A.; Kressler, J. *Macromol. Rapid Commun.* **2008**, *29*, 1140–1146.

(15) Opsteen, J. A.; van Hest, J. C. M. *Chem. Commun.* **2005**, 57–59.

(16) Gousse, C.; Gandini, A. *Polym. Int.* **1999**, *48*, 723–731.

(17) (a) Yuan, J. Y.; Pan, C. Y. *Eur. Polym. J.* **2002**, *38*, 1565–1571. (b) Drzal, P. L.; Shull, K. R. *Macromolecules* **2003**, *36*, 2000–2008. (c) Bielawski, C. W.; Morita, T.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 678–680.

(18) (a) Shipp, D. A.; Wang, J. L.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 8005–8008. (b) Tong, J. D.; Moineau, G.; Leclère, Ph.; Bredas, J. L.; Lazzaroni, R.; Jerome, R. *Macromolecules* **2000**, *33*, 470–479.

(19) Gauthier, M. A.; Gibson, M. I.; Klok, H. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 48–58.

(20) Jud, K.; Kausch, H. H. *Polym. Bull.* **1979**, *1*, 697–707.

(21) Liu, Y. L.; Chen, Y. W. *Macromol. Chem. Phys.* **2007**, *208*, 224–232.

(22) (a) Iris, Y.; Lobb, M. E. J.; Billingham, N. C.; Armes, S. P.; Lewis, A. L.; Lloyd, A. W.; Salvage, J. *Macromolecules* **2002**, *35*, 9306–9314. (b) Dong, C. M.; Sun, X. L.; Faucher, K. M.; Apkarian, R. P.; Chaikof, E. L. *Biomacromolecules* **2004**, *5*, 224–231.

(23) Sun, X. L.; Faucher, K. M.; Houston, M.; Grande, D.; Chaikof, E. L. *J. Am. Chem. Soc.* **2002**, *124*, 7258–7259.

(24) (a) Tong, J. D.; Leclere, P.; Rasmont, A.; Bredas, J. L.; Lazzaroni, R.; Jerome, R. *Macromol. Chem. Phys.* **2000**, *201*, 1250–1258. (b) Jeusette, M.; Leclere, P.; Lazzaroni, R.; Simal, F.; Vaneecke, J.; Lardot, T.; Roose, P. *Macromolecules* **2007**, *40*, 1055–1065.

(25) (a) Ban, H. T.; Kase, T.; Kawabe, M.; Miyazawa, A.; Ishihara, T.; Hagihara, H.; Tsunogae, Y.; Murata, M.; Shiono, T. *Macromolecules* **2006**, *39*, 171–176. (b) Zhang, K.; Zhibin, Y.; Subramanian, R. *Macromolecules* **2008**, *41*, 640–649.

(26) Odian, G. G. *Principle of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 2004; pp 373−374.

(27) (a) Rajan, M.; Agarwal, U. S.; Bailly, C.; George, K. E.; Lemstra, P. J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 575–583. (b) Jo, S. M.; Lee, W. S.; Ahn, B. S.; Park, K. Y.; Kim, K. A.; Paeng, I. S. R. *Polym. Bull.* **2000**, *44*, 1–8.

(28) (a) Villarroya, S.; Zhou, J.; Duxbury, C. J.; Heise, A.; Howdle, S. M. *Macromolecules* **2006**, *39*, 633–640. (b) Qin, S.; Saget, J.; Pyun, J.; Jia, S.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 8969–8977.

(29) (a) Klaikherd, A.; Ghosh, S.; Thayumanavan, S. *Macromolecules* **2007**, *40*, 8518–8520. (b) Zhao, H.; Shipp, D. A. *Chem. Mater.* **2003**, *15*, 2693–2695. (c) Mittal, A.; Sivaram, S.; Baskaran, D. *Macromolecules* **2006**, *39*, 5555–5558. (d) Chang, C.; Pugh, C. *Macromolecules* **2001**, *34*, 2027–2039.

(30) (a) Street, G.; Illsley, D.; Holder, S. J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1129–1143. (b) Chatterjee, D. P.; Mandal, B. M. *Macromolecules* **2006**, *39*, 9192. (c) Datta, H.; Bhowmick, A. K.; Singha, N. K. *Polymer* **2009**, *50*, 3259–3268.

(31) (a) Kavitha, A. A.; Singha, N. K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4441–4449. (b) Kavitha, A. A.; Singha, N. K. *Macromol. Chem. Phys.* **2007**, *208*, 2569–2577.

(32) Varshney, S. K.; Kesani, P.; Agarwal, N.; Zhang, J. X. *Macromolecules* **1999**, *32*, 235–237.

(33) Kear, K. E. *Developments in Thermoplastic Elastomers*, 3rd ed.; *Rapra Rev. Rep.* **2003**, *14*, 19.

(34) (a) Wool, P. R.; O'Connor, K. M. *Polym. Eng. Sci.* **1981**, *21*, 970–977. (b) McGarel, O. J.; Wool, R. P. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 2541–2560.

(35) (a) Gennes, D. P. G.; Seances, H. *Acad. Sci, Ser. B* **1980**, *291*, 219–221. (b) Prager, S.; Tirrell, M. *J. Chem. Phys.* **1981**, *75*, 5194–5198.

(36) (a) Kim, Y. H.; Wool, R. P. *Macromolecules* **1983**, *16*, 1115–1120. (b) Yang, F.; Pitchumani, R. *Macromolecules* **2002**, *35*, 3213–3224.

(37) (a) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R. *Science* **2002**, *295*, 1698–1702. (b) Tarducci, C.; Badyal, J. P.S.; Brewerb, S. A.; Willisb, C. *Chem. Commun.* **2005**, 406–408.

(38) Katti, A.; Shimpi, N.; Roy, S.; Lu, H.; Fabrizio, E. F.; Dass, A.; Capadona, L. A.; Leventis, N. *Chem. Mater.* **2006**, *18*, 285–296.

(39) Hugh, J. Mc. Thesis, Ultrasound Technique for the Dynamic Mechanical Analysis (DMA) of Polymers, Longford, Ireland, **2008**; pp 63−64.