"Click Chemistry" in Tailor-Made Polymethacrylates Bearing Reactive Furfuryl Functionality: A New Class of Self-Healing Polymeric Material

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ABSTRACT This investigation reports the effective use of the Diels–Alder (DA) reaction, a "click reaction" in the preparation of thermally amendable and self-healing polymeric materials having reactive furfuryl functionality. In this case, the DA and retro-DA (rDA) reactions were carried out between the tailor-made homo- and copolymer of furfuryl methacrylate prepared by atom-transfer radical polymerization and a bismaleimide (BM). The kinetic studies of DA and rDA reactions were carried out using Fourier transform infrared spectroscopy. The DA polymers were insoluble in toluene at room temperature. When the DA polymers were heated at 100 °C in toluene, it was soluble. This is because of the cleavage between furfuryl functionality and BM. The chemical cross-link density was determined by the Flory–Rehner equation. The cross-linked polymer showed much greater adhesive strength at room temperature, but the adhesive strength was quite low at higher temperature. The self-healing capability was studied by using scanning electron microscopy analysis. The thermal and dynamic mechanical properties of the thermally amendable cross-linked materials were investigated by thermogravimetric analysis and dynamic mechanical analysis.

KEYWORDS: Diels–Alder reaction • retro-Diels–Alder reaction • self-healing • thermoreversible

INTRODUCTION

The potential of "click chemistry" for materials synthesis has been increasingly recognized and has already resulted in the development of a wide range of interesting materials. Because of their high selectivity, high yields, and exceptional tolerance toward a wide range of functional groups and reaction conditions, click reactions have recently attracted increased attention in polymer synthesis as well as polymer modification. Diels–Alder (DA) click reactions have played an essential role in various aspects of polymer synthesis and chemical modification of the polymers (1). The use of polymeric systems based on acrylic derivatives as biomaterials for clinical applications has increased because of their excellent biocompatibility and long-term stability (2). Nowadays, there is a considerable interest in the synthesis of new types of polymeric materials and also in the modification of existing polymers in order to alter their properties to meet requirements for new applications (3). Recently, the DA reaction based on macromolecular chemistry has attracted much attention, particularly for providing new materials (4–13). The thermoreversibility of the DA reaction is an interesting feature. The DA reaction between diene and dienophile forms covalent bonds, which could be easily cleaved on heating. The equilibrium of the DA reaction could be displaced toward the reagents by heating through the retro-DA (rDA) reaction (14–23). Utilization of the DA reaction in polymer cross-linking to build up the polymer networks results in a new class of thermally reversible cross-linked polymers. In recent years, these thermally reversible cross-linked polymers are widely studied to explore applications in encapsulants, structural materials, coatings, etc. For example, a semiconductor can be redeemed from bad encapsulation by using such polymers as encapsulants; self-repairing polymeric materials made with these kinds of polymers can be used as smart materials (24).

To the best of our knowledge, there is no report on DA "click chemistry" in the mechanical, solution, thermal, and self-healing properties of the tailor-made polymethacrylates bearing reaction of furfuryl functionality. This investigation reports the preparation of a DA polymer based on the homo- and copolymer of furfuryl methacrylate as a diene and maleimide as a dienophile and the kinetics of the DA and rDA reactions. In this case, polymers having furfuryl functionality were prepared via atom-transfer radical polymerization (ATRP) as well as via conventional free-radical polymerization (FRP) and their performances toward DA reactions were compared. This investigation also reports the mechanical as well as the thermal properties of the cross-linked polymers. Scheme 1 outlines our synthetic strategy to the various phases of this work, the preparation of a poly(furfuryl methacrylate)–bismaleimide adduct by the DA reaction, and thermoreversible de-cross-linking by the rDA reaction. The self-healing property of these polymers has also been studied by scanning electron microscopy (SEM) analysis.

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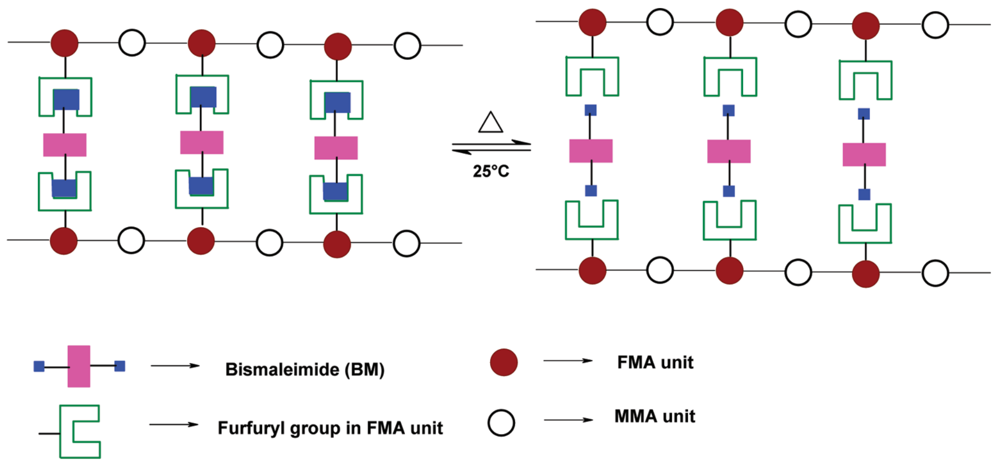
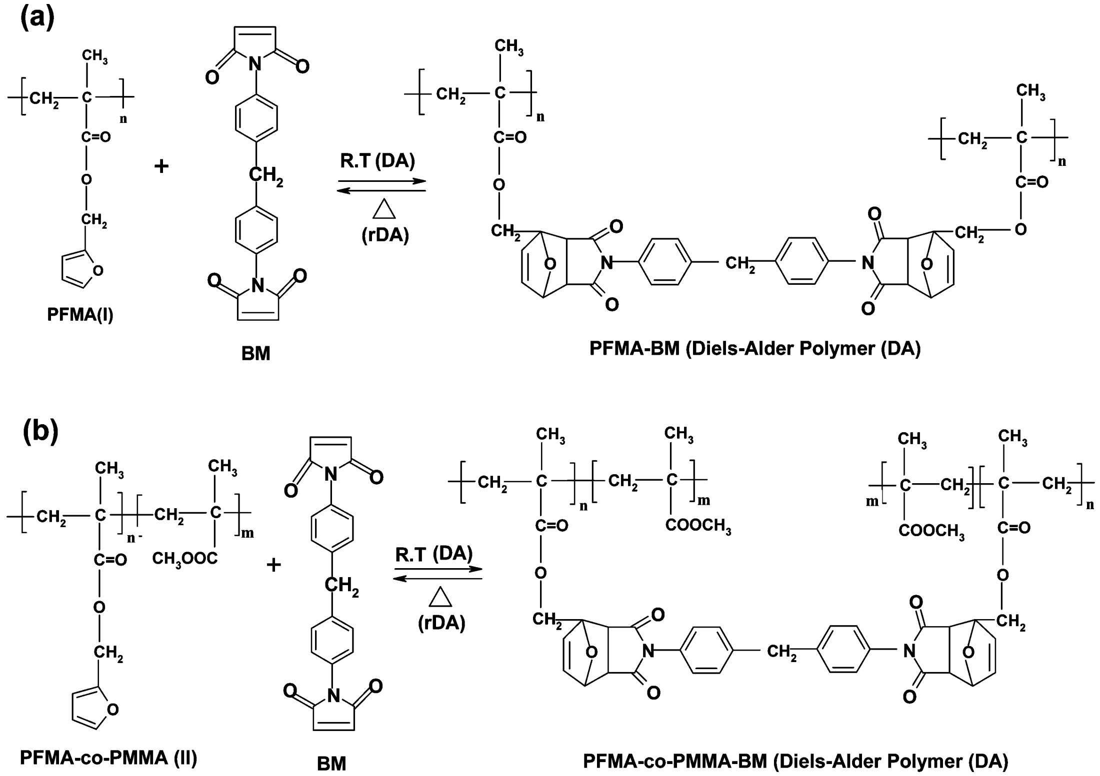
Scheme 1. General Presentation of a Thermally Amendable Polymer by DA "Click Chemistry"



Scheme 2. Preparation of Thermally Amendable Cross-Linked Polymers (a) PFMA−BM and (b) PFMA-*co*-PMMA−BM



EXPERIMENTAL SECTION

Materials. Furfuryl methacrylate (FMA; 97%, Aldrich, Milwaukee, WI) and methyl methacrylate (MMA; 99%, Aldrich, Milwaukee, WI) were purified by vacuum distillation and stored in a refrigerator. Conventional FRP was carried out according to standard procedures (25). The solvents, toluene and dichloromethane (SD Fine chemicals, Mumbai, India), were purified according to standard procedures (26). CuCl (Aldrich, Milwaukee, WI) was purified by washing with glacial acetic acid, followed by diethyl ether, and then dried under vacuum. Ethyl 2-bromoisobutyrate (EBiB; 98%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA; 97%), and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BM; 95%) were obtained from Aldrich (Milwaukee, WI) and used as received.

Synthesis of Poly(furfuryl methacrylate) (PFMA) by the ATRP Process. In a typical experiment, CuCl (0.020 g, 2.01 × 10^{-4} mol), HMTETA (0.046 g, 2.01 × 10^{-4} mol), FMA (2.00 g, 1.20 × 10^{-2} mol), and toluene (6 mL) were taken in a 100-mL three-necked, round-bottom flask. The flask was closed with a silicon rubber septum in one neck, and another neck was equipped with a condenser. The polymerization was started by adding EBiB (0.039 g, 2.01 × 10^{-4} mol) and was carried out at 90 °C under a nitrogen atmosphere. A conversion of 63% was obtained at 12 h. The polymer was purified by passing through an alumina column to remove the catalyst and then was dried in a vacuum oven at 45 °C. A part of the polymer sample was analyzed by gel permeation chromatography (GPC) to determine its molecular weight and molecular weight distribution. ^{1}H NMR: δ 1.5−2.0 (−CH_3 and >CH_2 protons of the main-chain backbone), 5.0 (s, 2H, −OCH_2−), 6.4 (m, 2H, =$CHCH$= of the furan ring), 7.4 (s, 1H, =CHO− of the furan ring). M_n(GPC) and M_w/M_n of the polymer were 6544 and 1.31, respectively.

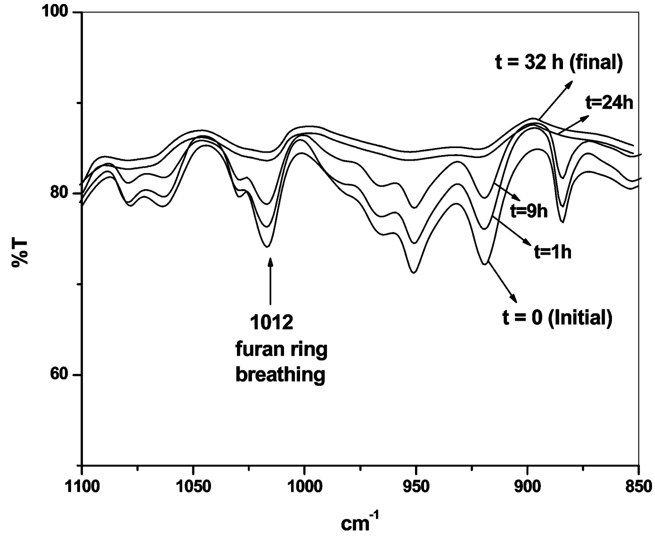


FIGURE 1. FTIR spectra of the DA reaction of polymer PFMA−BM at different time intervals.

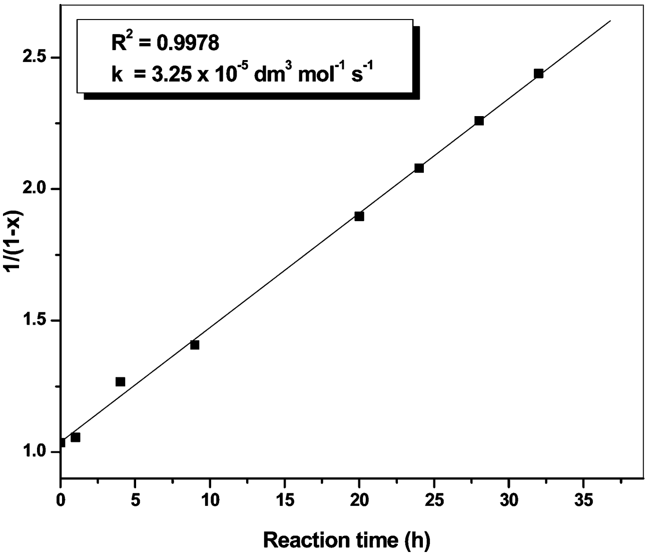


FIGURE 2. Second-order kinetic plot for the DA reaction between PFMA and BM (eq 4).

Synthesis of Poly(furfuryl methacrylate)-*co*-poly(methyl methacrylate) (PFMA-*co*-PMMA) by the ATRP Process. Synthesis of the copolymer was carried out in a feed ratio of 60:40 of FMA and MMA, respectively. For synthesis of the copolymer, a method similar to that described for the homopolymerization of PFMA was followed. In this case, two different monomers are used: FMA (2.00 g, 1.20×10^{-2} mol) and MMA (0.802 g, 8.02×10^{-3} mol). A conversion of 70% was reached at 11 h. ^{1}H NMR: δ 0.9−1.9 ($-CH_3$ and $>CH_2$ protons of the main-chain backbone), 3.5 (s, 3H, $-OCH_3$ of PMMA), 4.9 (s, 2H, $-OCH_2-$ of PFMA), 6.3 (m, 2H, $=CHCH=$ of the furan ring), 7.4 (s, 1H, $=CHO-$ of the furan ring). The copolymer has 65% FMA and 35% MMA, as determined by ^{1}H NMR. M_n(GPC) and M_w/M_n of the polymer were 10 060 and 1.31, respectively.

Preparation of Thermally Reversible Cross-Linked Polymers (DA Reaction). PFMA and BM (1:1 by mole) in an equal mole ratio were dissolved in 4 mL of dichloromethane (CH_2Cl_2) and were stirred at room temperature for 32 h. The resultant cross-linked polymer was dried in a vacuum oven for 12 h. Yield: 1.23 g (79%). FTIR (KBr, cm^{-1}): 3428, 2957, 1713, 1636, 1394, 1260, 824, 667.

rDA Reaction. All rDA reactions were carried out at different temperatures. Typically, 0.2 g of DA polymer (**I**) was placed in 1 mL of toluene and heated at 100 °C for 9 h. The resulting product was completely soluble in the solvent. Five different temperatures were used in order to study the rDA reaction. This reaction was characterized by Fourier transform infrared (FTIR) analysis.

Characterization and Methods. ***Structural Characterization. NMR Spectroscopy.*** ^{1}H NMR spectra of polymers were recorded using a 300 MHz Bruker NMR spectrometer, using $CDCl_3$ as the solvent, which had a small amount of tetramethylsilane as an internal standard.

FTIR. Kinetic studies of DA as well as rDA reactions were carried out using a Perkin-Elmer, Inc., version 5.0.1 spectrophotometer. In this case, the polymer solution in $CHCl_3$ was film cast over KBr cells, and then the FTIR spectra were recorded. IR spectra were recorded in the range of 4000−400 cm^{-1}.

Thermal Analysis. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGA instrument [model: Pyris Diamond TG/DTA] by heating the polymer sample from 30 to 800 °C at a programmed heating rate of 20 °C min^{-1}.

Mechanical Properties. The tests for the adhesive strength were carried out on a Hounsfield H10KS UK, according to ASTM-D-1002. In this case, equal amounts of polymer (PFMA or PFMA-co-PMMA) and BM (by weight) were dissolved in tetrahydrofuran to get 25% of the solid content in the solution. The polymer solution was applied on the two wooden substrates (125 mm × 25 mm × 6 mm each) to get a 25 × 25 mm contact area and a bond thickness of 1 mm. The adhesive joint was then obtained by pressing two wooden substrates at a pressure of 10 kgf. The mechanical strength was determined in the lap shear mode at 120 °C as well as at room temperature (25 °C). The Hounsfield Instrument had a provision of measuring the mechanical properties at room temperature as well as at higher temperatures.

Measurement of the Swelling Ratio of Cross-Linked Polymers. The swelling ratio of the polymer was calculated from the equation

$$\text{swelling ratio (\%)} = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

where W_d is the dry sample weight and W_s is the weight of the swollen sample.

Chemical Cross-Link Density (CLD). The CLD of the cross-linked polymers (PFMA−BM and PFMA-*co*-PMMA−BM) was determined by following the procedure of "equilibrium swelling" in toluene at room temperature (27). The volume fraction of the polymer was calculated from the swollen and deswollen weights using the relation

$$V_r = \frac{(D - FT)/\rho_r}{(D - FT)/\rho_r + A_0/\rho_s} \qquad (2)$$

where T is the original weight of the cross-linked polymer, D is the deswollen weight, F is the weight fraction of insoluble components, A_0 is the weight of the absorbed solvent, and ρ_r and ρ_s are the densities of the polymer and solvent, respectively. The CLD was calculated using the Flory−Rehner equation (27).

$$\rho_c = \frac{-[\ln(1 - V_r) + V_r + \xi V_r^{\,2}]}{2V_0[V_r^{\,1/3} - V_r/2]} \qquad (3)$$

where ρ_c = CLD of the polymer, V_0 = molar volume of toluene (9.4309×10^{-3} cm^3 mol^{-1}) (28), V_r = volume fraction of the

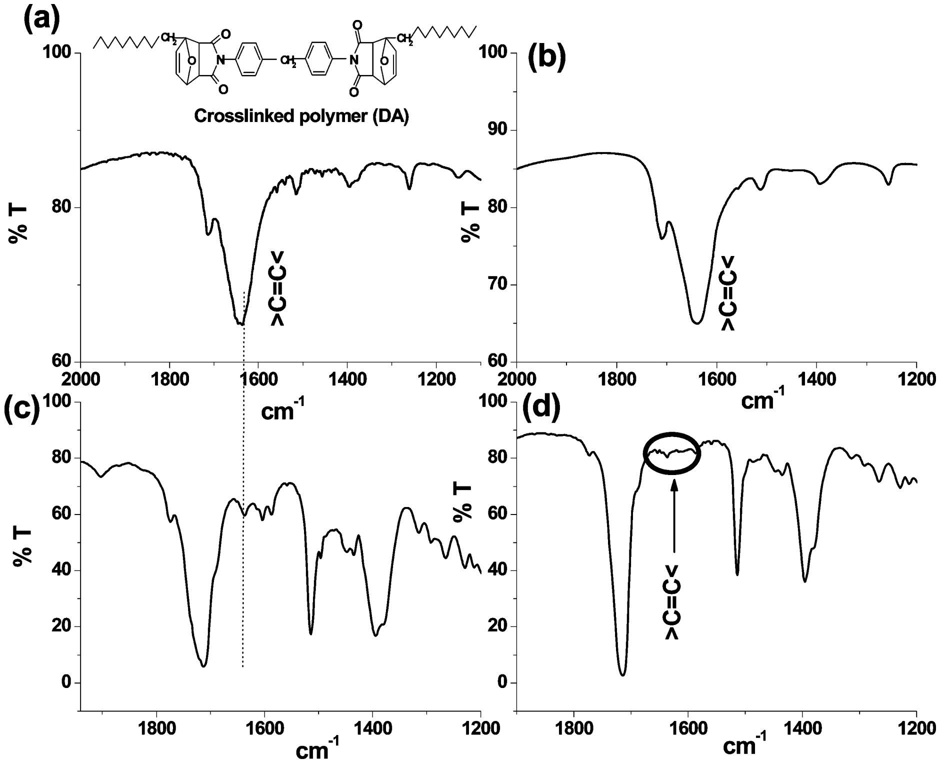


FIGURE 3. FTIR spectra of the rDA reaction in the cross-linked polymer PFMA−BM in toluene at 100 °C at different times: (a) $t = 0$ h; (b) $t = 2$ h; (c) $t = 4$ h; (d) $t = 9$ h.

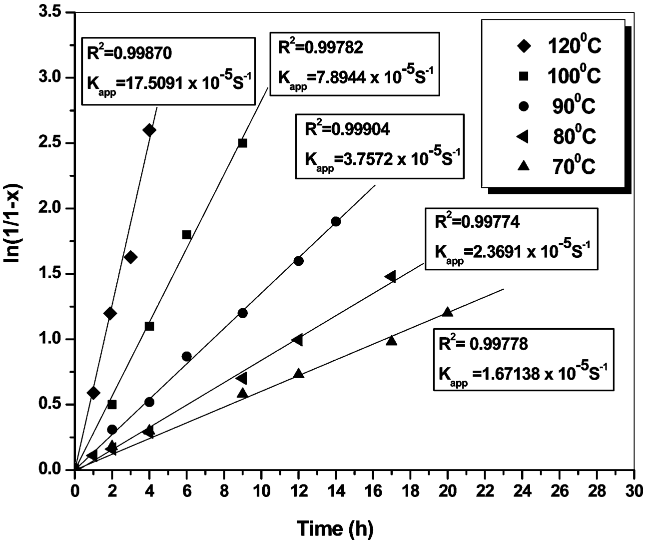


FIGURE 4. First-order kinetic plot for the rDA reaction of the cross-linked polymer PFMA−BM (eq 5): (◆) 120 °C; (□) 100 °C; (●) 90 °C; (tilted ▲) 80 °C; (▲) 70 °C.

Table 1. Rate Constant (*k*) for the rDA Reaction of the Cross-Linked Polymer PFMA−BM at Different Temperatures

temperature (°C)	R^2	k_{app} (10^{-5} S^{-1})
120	0.9987	17.51
100	0.9978	7.89
90	0.9990	3.75
80	0.9977	2.37
70	0.9977	1.67
50	no change (absence of rDA)	

cross-linked polymer in a swollen sample, and ξ = polymer−solvent interaction parameter (0.53) (29).

SEM. The healing nature of the cross-linked polymer was studied using surface morphological images by a JEOL JSM 850 scanning electron microscope. A scratch was deliberately made on the film surface and then placed at 120 °C for 4 h. The samples were characterized at regular intervals by SEM analysis.

Dynamic Mechanical Analysis (DMA). DMA properties such as the storage modulus (E'), loss modulus (E''), damping factor (tan δ), and dynamic viscosity of the DA cross-linked polymer were measured in a TA Instruments model DMA 2980. The effect of the frequency on the viscoelastic properties of the polymers was performed in compression mode (applied by two parallel circular plates of 16.97-mm diameter and a sample thickness of 0.3 mm). The top stationary plate was clamped rigidly, while the bottom plate was oscillated in the vertical direction by the motor connected to the plate. The separation between the plates was controlled electronically. A strain sweep test was first performed to select the appropriate strain amplitude at which the linear viscoelastic behavior was observed. This test was carried out by keeping the frequency constant at 1 Hz, and the strain ranged from 0.025% to 6.0% at various temperatures of 80, 100, 120 and 140 °C. A strain amplitude of 15 μm was selected for further frequency sweep measurements. Tests were carried out as a function of the frequency from 0.1 to 50 Hz, keeping the strain constant at 15 μm.

RESULTS AND DISCUSSION

The tailor-made polymers having furfuryl functionality were prepared by the homopolymerization of FMA as well as the copolymerization of FMA with MMA by ATRP. In this case, the DA reactions between BM and the furfuryl functional groups lead to a well-defined cross-linked polymer in which the main-chain segments are the tailor-made PFMA or its copolymer with MMA (PFMA-*co*-PMMA). The overall synthesis has been illustrated in Scheme 2.

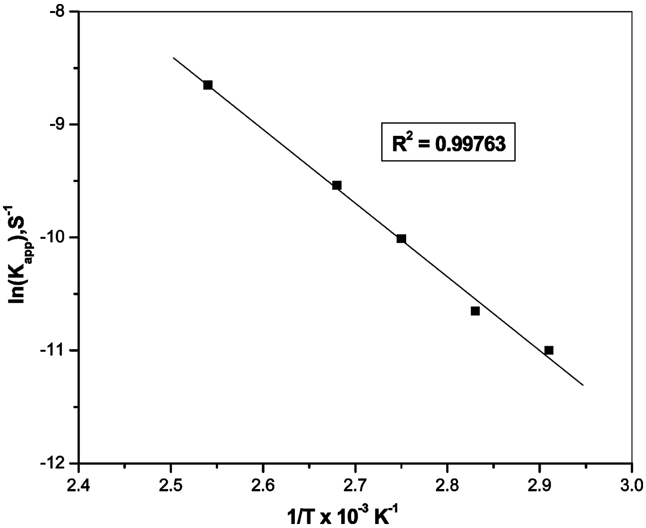
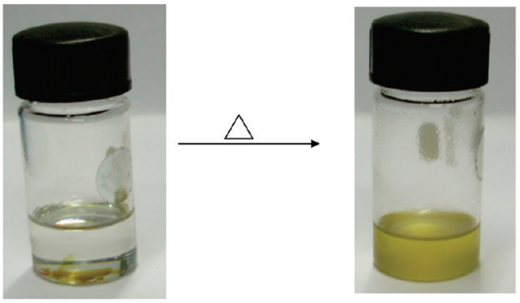
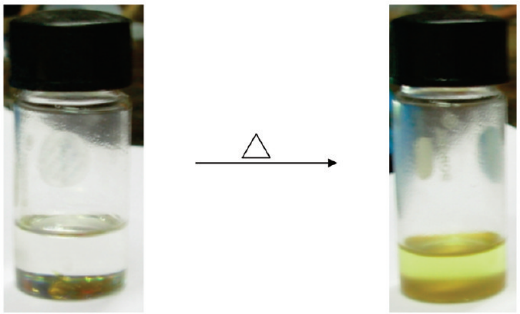


FIGURE 5. Arrhenius plot correlating the rate constant with temperature for the rDA reaction of the cross-linked PFMA−BM.


(a) Crosslinked PFMA-BM in toluene at 25 °C (insoluble)

(b) Crosslinked PFMA-BM in toluene at 100 °C, 9h, (Soluble)


(c) Crosslinked PFMA-co-PMMA-BM in toluene at 25 °C (insoluble)

(d) Crosslinked PFMA-co-PMMA-BM in toluene at 100 °C, 9h, (soluble)

FIGURE 6. Photographs of observation of the thermally reversible cross-linking behavior of PFMA−BM and PFMA-*co*-PMMA−BM polymers.

Kinetic Study of the DA and rDA Reactions. The kinetics of the DA cross-linking reaction of PFMA−BM were followed by monitoring of the FTIR spectra at different time intervals. Figure 1 shows the time-dependent changes of the absorption peak at 1012 cm^{-1}, which is due to furan ring breathing. The band of >C═O at 1713 cm^{-1} was used as the reference peak. In this case, the ratio of intensities at 1012 and 1713 cm^{-1} (I_{1012}/I_{1713}) was monitored at different time intervals. The ratios of intensities at the start of the DA reaction and at time t are designated by N_0 and N_t, respectively. The plot of $(1 - x)^{-1}$ versus time was linear [where $x = (N_0 - N_t)/N_0$], indicating the DA reaction followed second-order kinetics. The linear least-squares analysis showed a value of 0.9978 for R^2. So, the rate equation can be expressed as

Table 2. Swelling Properties of the Cross-Linked Polymers of PFMA and PFMA-*co*-PMMA with BM

polymer	chemical CLD at room temperature, mol cm^{-3}	heating at 100 °C
PFMA	70.98	soluble
PFMA-*co*-PMMA (20:80)	108.16	soluble
PFMA-*co*-PMMA (50:50)	156.31	soluble
PFMA-*co*-PMMA (60:40)	108.86	soluble
PFMA-*co*-PMMA (80:20)	99.23	soluble

$$\frac{1}{1 - x} = kt \tag{4}$$

The rate constant k for the DA reaction of PFMA with BM was calculated to be 3.25 × 10^{-5} dm^3 mol^{-1} s^{-1} from the slope of the plot as shown in Figure 2. Goiti et al. (23) prepared the copolymer of styrene and FMA and studied its DA reaction. They reported k of 1.91 × 10^{-5} dm^3 mol^{-1} s^{-1} of the DA reaction of PFMA prepared by conventional radical polymerization. In our case, we observed higher k, which indicated a faster DA reaction and higher reactivity of tailor-made PFMA toward the DA reaction between furfuryl functionality and BM moieties. The conventional radical polymerization of FMA leads to severe gelation during polymerization because of several side reactions (23). This leads to polymers with uncontrolled molecular weights and with very broad polydispersity indices (PDI), which restrict the mobility of diene and dienophile inside the polymer matrix. In our study, we prepared the polymer by ATRP. Interestingly, these polymers were gel-free and had low PDIs, which indicated that there was no side reaction involving the furfuryl functionality (25). So, the DA reaction between the furfuryl functionality and BM was fast, and the rate constant (k) was higher.

The scheme of the rDA reaction is shown in Scheme 2. The kinetics of the rDA reaction were followed by FTIR spectroscopy (Figure 3). Figure 3a shows the FTIR spectra of the cross-linked DA polymers. Figure 3b−d are FTIR spectra of the cross-linked polymers at different intervals of time heated at 100 °C in toluene. Figure 3a shows a peak at 1636 cm^{-1} attributed to >C═C< that appears to be due to the DA reaction between PFMA and BM. Figure 3 indicates that there is no difference between Figure 3a and b of Figure 3, which represent the FTIR spectra of the PFMA−BM adduct heated at 100 °C at $t = 0$ and 2 h, respectively. However, in parts c and d of Figure 3 (FTIR spectra at $t = 4$ and 9 h, respectively), the peak at 1636 cm^{-1} slowly disappears. This indicates that the cleavage of bonds between the furfuryl group and BM is due to the rDA reaction, as shown in Scheme 2. The kinetic study was performed by monitoring the peak intensities of >C═O and >C═C< (at 1723 and 1636 cm^{-1}, respectively) at different time intervals. The integrated rate expression for first-order kinetics can be expressed as

$$\ln\left(\frac{1}{1-x}\right) = kt \qquad (5)$$

The linear kinetic plot of the rDA reaction follows first-order kinetics (Figure 4). The linear least-squares analysis gives the values for R^2 of different kinetic plots. The rate constant k for the rDA reaction of the PFMA–BM adduct was calculated from the slope of the kinetic plot as shown in Figure 4. Table 1 shows the values of k calculated at different temperatures. Figure 5 shows the Arrhenius plot of $\ln(k_{\mathrm{app}})$ versus $1/T$, and from the slope of this plot, an apparent enthalpy of activation (E_a) of 54.25 kJ mol^{-1} for the rDA reaction was calculated. The rDA reaction for the simple organic molecules also follows first-order kinetics, and their k values are reported in the literature (30, 31). Goiti et al. (20) reported the kinetic study of the rDA reaction of a PFMA–PS–BM copolymer adduct in which the polymer PFMA was already severely cross-linked because it was prepared by conventional radical polymerization. This cross-linked polymer (PFMA–PS–BM) was severely gelled, and they found a low activation energy of 21 kJ mol^{-1} of the rDA reaction (20).

Solution Properties of the Cross-Linked Polymers. The solution properties of the cross-linked PFMA–BM adducts were studied in toluene at 25 °C as well as at higher temperatures. Figure 6 indicates that the cross-linked polymer is not soluble at 25 °C (Figure 6a) and it is only swollen, indicating the cross-linking reaction between PFMA and BM. When it was heated at 100 °C, it was soluble (Figure 6b), indicating the cleavage of the furfuryl ring and BM. When the solvent was evaporated slowly from the solution, the resultant solid PFMA–BM adduct was cross-linked again. Upon addition of toluene, the material was not soluble any more (Figure 6a). A similar observation was made in the case of the copolymer of PFMA-*co*-PMMA (Figure 6c,d). Table 2 shows the swelling properties of the thermoreversible cross-linked polymer in toluene. The CLD of the cross-linked polymers was determined by the Flory–Rehner equation (27). The CLD of the PFMA–BM adduct is 70.98 mol cm^{-3}. In the copolymer, the CLD first increases with an increase in the PFMA content (Table 2), which is due to a greater extent of cross-link formation due to the availability of more furfuryl functionality. However, the CLD decreases when the PFMA content is more than 50%. This may be due to the intramolecular DA reaction between BM and furfuryl functionality present in the same PFMA macromolecuar chain. For the same reason, the homopolymer of FMA (i.e., PFMA) also has a lower CLD. In this case, the intramolecular DA reaction is favored because the furfuryl functionality is present in every alternate carbon atom. The intramolecular DA reaction does not contribute to the CLD because it happens in the same macromolecular chain. However, at this point it is difficult to quantify the extent of the intramolecular DA reaction.

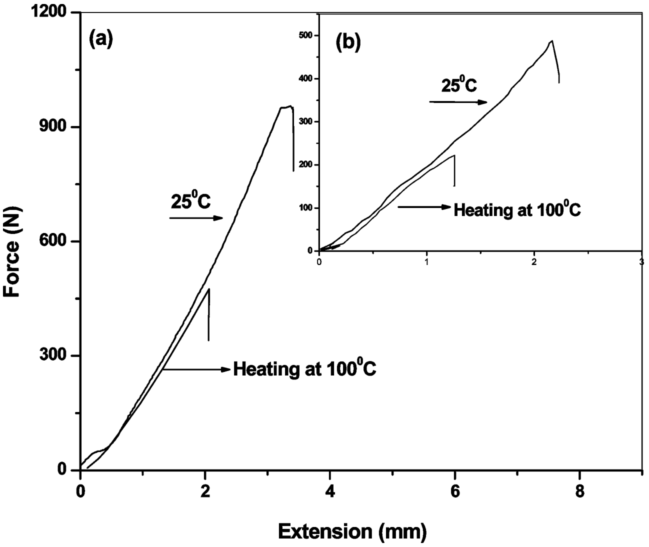


FIGURE 7. Lab shear stress plot of cross-linked polymer at low and high temperature: (a) cross-linked PFMA-*co*-PMMA–BM; (b) cross-linked PFMA–BM copolymers.

Mechanical Properties of the Thermoreversible Cross-Linked Polymer at High as Well as at Low Temperature. The mechanical properties of PFMA, PFMA–BM, and PFMA-*co*-PMMA hybrid were determined in terms of the adhesive strength by applying them between two wooden substrates in the film form. The properties were measured at room temperature (25 °C) as well as at high temperature (100 °C), and they are tabulated in Table 3. This shows that the adhesive strength of PFMA–BM and PFMA-*co*-PMMA–BM hybrid materials at room temperature (25 °C) is much higher than the strength

Table 3. Mechanical Properties of the Polymers of FMA with and without BM at Low and High Temperatures

	adhesive strength (MPa)			
	without BM		cross-linked with BM	
polymer[a]	room temperature (25 °C)	at higher temperature (100 °C)	room temperature (25 °C)	at higher temperature (100 °C)
PFMA	9.8	9.0	20	11
PFMA-*co*-PMMA (20:80)	15.1	14.9	31.2	17.5
PFMA-*co*-PMMA (50:50)	16.3	16.2	33.2	15.1
PFMA-*co*-PMMA (60:40)	18.1	17.8	35.2	20
PFMA-*co*-PMMA (80:20)	13.3	13.8	35.8	15.4

[a] In this case, all of the polymers were prepared by ATRP by using a CuCl/HMTETA catalyst and ligand.

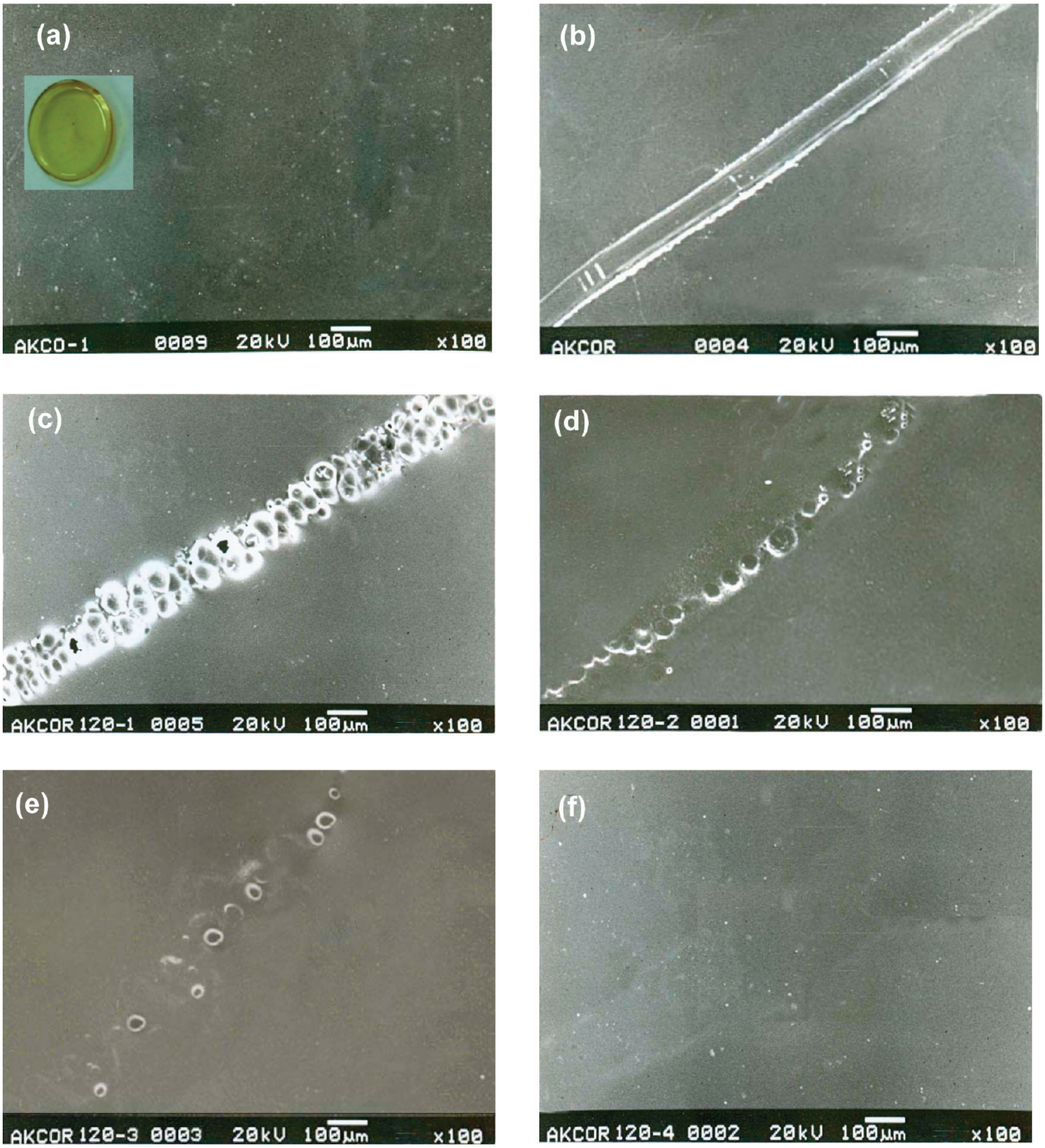


FIGURE 8. Self-healing study of cross-linked polymer PFMA—BM. SEM micrographs of (a) the cross-linked polymer and (b) the knife-cut sample. (c—f) Thermally self-repaired sample of cross-linked polymer PFMA—BM at 1, 2, 3, and 4 h, respectively.

of these materials at higher temperature (100 °C). Figure 7a and b show the representative load versus extension curves of the homo- and copolymer specimens at 25 °C as well as at 100 °C. This shows that the adhesive strength fails much earlier in the case of the polymer at 100 °C than the polymer at 25 °C. The "intermonomer" linkages were formed by the DA cycloaddition reaction at 25 °C, so the strength is higher (20 and 35.2 MPa for homo- and copolymer, respectively). However, the linkages disconnect at 100 °C, leading to much lower strength (11 and 20.1 MPa for homo- and copolymer, respectively). The decrease in the adhesive strength in the case of cross-linked homopolymers is due to more intramolecular DA reactions, which were corroborated from the measurement of the CLD as explained earlier. PFMA and PFMA-*co*-PMMA prepared by conventional radical polymerization by using benzoyl peroxide could not be applied to the substrate because it was insoluble in organic solvents because of severe gelation.

Self-Healing Characteristics of the Cross-Linked Polymer. The self-healing property of cross-linked polymer PFMA—BM was followed by SEM analysis (Figure 8). The film of the cross-linked materials shows a very smooth and planar surface (Figure 8a). A notch was made on the PFMA—BM film surface using a knife (Figure 8b). When the knife-cut sample was heated at 120 °C (Figure 8c—e), the cleavage of the covalent bonds occurs slowly because of rDA in the cross-linked polymer. Because of the cleavage of the bonds

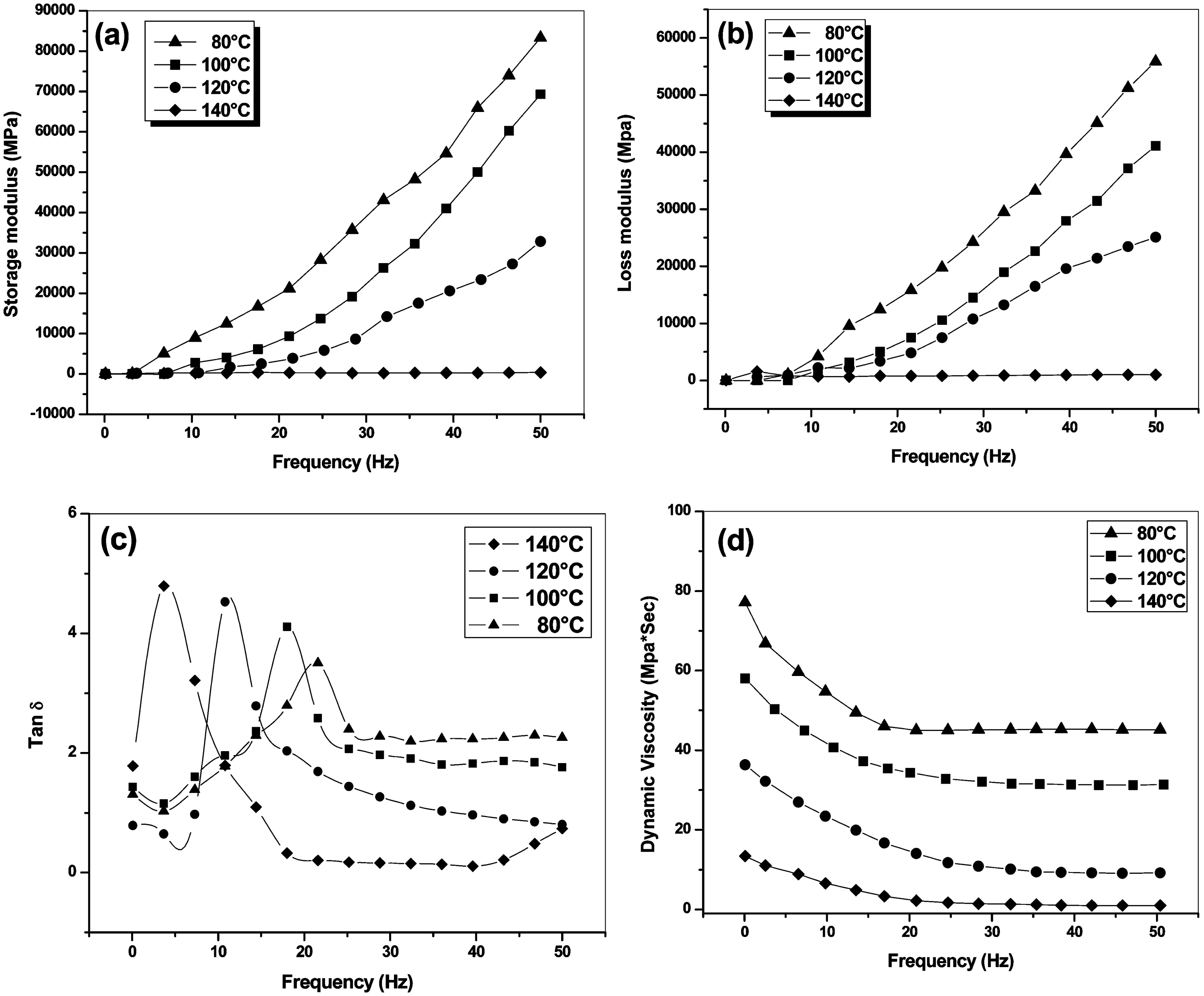


FIGURE 9. Dynamic mechanical spectra of a PFMA–BM adduct: (a) storage modulus as a function of the strain frequency; (b) loss modulus as a function of the strain frequency; (c) damping factor (tan δ) as a function of the strain frequency; (d) dynamic viscosity as a function of the strain frequency.

between the furfuryl group and BM, the materials slowly get enhanced mobility, as shown in Figure 8c–e. Finally, Figure 8f shows that the polymer self-heals to show a complete notch recovery to regain its earlier structure (Figure 8a).

DMA. Figure 9a shows the effect of the frequency on the storage modulus (E') of the cross-linked polymers (PFMA–BM) at different temperatures of 80, 100, 120, and 140 °C. As the frequency increased, the storage modulus (E') was found to increase. At lower frequencies, the viscoelastic polymeric chains get much time for molecular relaxation. As the frequency increases, the time for such relaxation decreases, resulting in an increase in the modulus of the polymeric chains (32). The effect of the frequency on the loss modulus (E''), as depicted in Figure 9b, was found to follow the same trend as that on the storage modulus. At a given frequency, E' and E'' have the lowest value at 140 °C. This indicates that the cross-linked DA polymer becomes softened at higher temperature. It was also found that both E' and E'' decreased with increasing temperature. The decrease in the modulus is attributed to the cleavage of reversible DA cross-links at higher temperatures. These bonds are expected to re-form at lower temperatures, and this fact is supported by the higher values of E' and E'' at 80 °C (Figure 9a,b). Figure 9c shows the damping factor (tan δ) as a function of the frequency. The tan δ peak height was found to increase with increasing temperature. Also, it was observed a shift toward lower frequency regions with increasing temperature. As the temperature was increased, the DA cross-links cleaved and the polymeric chains became more liberated for deformations. This is the cause for the increase in the peak height of the loss factor (tan δ) at higher temperatures. At higher temperatures, the more flexible polymeric chains deformed even at lower frequencies, which caused shifting of tan δ peaks toward lower frequencies.

Figure 9d shows the dynamic viscosity (η') as a function of the frequency. The dynamic viscosity was calculated from eq 6 (where E'' is the loss modulus and ω is the frequency) (33).

$$\eta' = \frac{E''}{\omega} \quad (6)$$

The dynamic viscosity of the cross-linked polymer was found to decrease with increasing frequency. The decrease was prominent at lower frequencies and tended to level off at higher frequencies. At lower frequencies, energy could be dissipated in viscous flow. However, as the oscillation frequency was increased, vibrations occurred too rapidly for the dissipation of energy by viscous flow. As a result, there was a reduction in the dynamic viscosity of the materials (34). The increase in the temperature reduced the dynamic viscosity of the DA polymer at a given frequency. The lowest value of the dynamic frequency was recorded at 140 °C for the polymer. This may be attributed to the breakage of thermoreversible cross-links in the polymeric network at higher temperature, which, in turn, enhances the flow. The reversibility of the DA cross-linked polymer is underlined by the viscosity study by DMA.

Thermal Properties of the Cross-Linked Polymer. The TGA of the cross-linked copolymers shows that the higher the cross-link density, the more thermally stable the material is. Figure 10 shows the TGA curves for homo- and copolymers of PFMA (prepared by ATRP as well as by conventional radical polymerization) analysis and their adduct with BM. Curves a and b in Figure 10 show the TGA curves of the homo- and copolymer of PFMA prepared by conventional radical polymerization using benzoyl peroxide as the initiator. The degradation process in the homo- and copolymers prepared by conventional radical polymerization occurs at several stages as a result of scission of the head-to-head linkages, end-chain initiation of the vinylic ends, and random scission of the polymer chain (35, 36). Figure 10c and d show the TGA curves of PFMA and PFMA-*co*-PMMA prepared by ATRP. This indicates that they have single as well as maximum degradation temperatures at 398 and 391 °C, respectively. This clearly indicates that the side reaction or the bimolecular terminations are minimized during ATRP. Interestingly, the TGA curves (curves e and f) show that the cross-linked DA polymers have higher thermal stability.

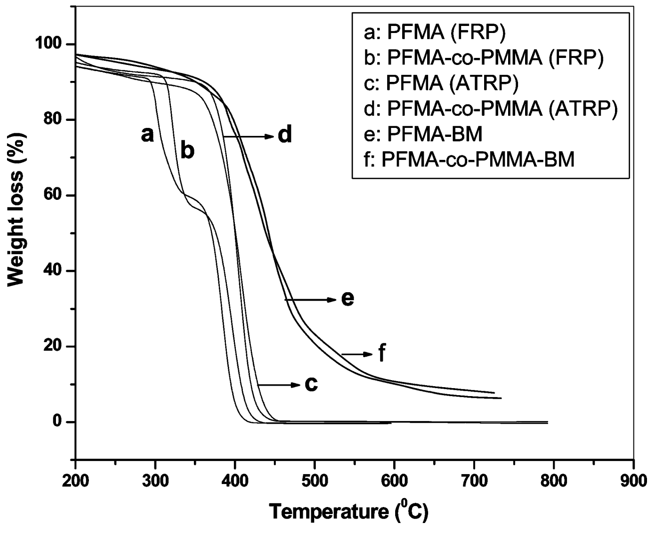


FIGURE 10. TGA analysis of the polymers (a) PFMA (FRP), (b) PFMA-*co*-PMMA (FRP), (c) PFMA (ATRP), (d) PFMA-*co*-PMMA (ATRP), (e) PFMA-BM, and (f) PFMA-*co*-PMMA—BM.

CONCLUSIONS

The thermally amendable cross-linked polymers were prepared successfully by DA reactions between BM and PFMA or PFMA-*co*-PMMA. When the polymers were heated over 100 °C, they were soluble because of the cleavage of the DA adduct by rDA reaction. The kinetic studies of the DA and rDA reactions were carried out using FTIR analysis for PFMA—BM adducts. The thermoreversible nature of the polymers was confirmed by the swelling as well as the mechanical properties of the polymer. The adhesive property of the cross-linked polymer at room temperature was greater than that of polymers at higher temperature. The self-healing property of PFMA—BM was studied by SEM analysis, and complete healing was observed in 4 h. DMA studies showed that E', E'', and the dynamic viscosity (η') decreased with an increase in the temperature. The TGA showed that the PFMA and its copolymer prepared by ATRP has a single degradation temperature and their DA adduct with BM has a higher degradation temperature. Interestingly, the mechanical, solution, and SEM studies confirmed the thermoreversible and self-healing character of the cross-linked PFMA—BM adducts. These materials can have potential applications in self-healing coatings and thermoreversible adhesives.

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