Self-Complementary Multiple Hydrogen Bonding Interactions Increase the Glass Transition Temperatures to Supramolecular Poly(methyl methacrylate) Copolymers

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ABSTRACT: We have prepared a series of poly(methyl methacrylate) (PMMA)-based copolymers through free radical copolymerization of methyl methacrylate in the presence of 2-ureido-4[1H]-pyrimidinone methyl methacrylate (UPyMA). The glass transition temperature was increased with the increase of UPyMA contents in PMMA copolymers due to strong self-complementary multiple hydrogen bonding interactions of UPy moiety. The Fourier transform infrared and solid-state NMR spectroscopic analyses provided positive evidence for the presence of multiple hydrogen bonds interaction of UPy moiety. Furthermore, the proton spin-lattice relaxation time in the rotating frame [$T_{1\rho}$(H)] for the PMMA copolymers had a single value that was less than pure PMMA, indicating the smaller domain sizes in PMMA copolymers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3275–3282, 2012

Key words: multiple hydrogen bonding; supramolecules; thermal property; PMMA copolymer

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a mass-produced, commercially available polymer with high light transmittance, chemical resistance, and weathering corrosion resistance and good insulation.[1] However, relative low glass transition temperature (T_g = ca. 100°C) limited the use in optical electronics industry, for materials such as compact discs (CD), optical glasses, and optical fibers, because it undergoes distortion when used in an inner glazing material. To raise the value of T_g, PMMA copolymers incorporating rigid or bulky monomer structures[2,3] or monomers that can form hydrogen bonds with the carbonyl groups of PMMA have been reported widely.[4–9] Previously, the copolymerization with methacrylamide (MAAM) through hydrogen bonding interactions can raise the value of T_g of PMMA[10–13] due to compositional heterogeneities in hydrogen bonded copolymers.[14,15] However, in these previous studies,[4–13] the monomers only possessed relatively weak single hydrogen bonding moieties and such intermolecular interactions must be present at relatively high mole percentages to enhance the thermal behavior of copolymers; therefore, the structures of the copolymers differ substantially from those of their unmodified polymers.[16–21] Ideally, adding low mole percentages of the recognition units into the copolymers would enhance their thermal properties.[21–35]

As a result, we reported another approach to raise the T_g value of PMMA through free radical copolymerizations of methyl methacrylate in the presence of the either 2-vinyl-4,6-diamino-1,3,5-triazine (VDAT) or vinylbenzylthymine (VBT).[36] The complementary multiple hydrogen bonding arrays between diamino-1,3,5-triazine (DAT) and thymine (T) can significantly increase the T_g value of PMMA copolymer mixtures. The inter-association equilibrium constant between DAT and T of ca. 890 M^{-1} has been reported.[37] Complementary multiple hydrogen bonding arrays play a fundamental role in complex biological systems (e.g., DNA duplexes). Mimicking the molecular recognition by biological system is one of the most attractive themes in contemporary science.[38] Taking this cue from Nature, we wondered whether we could enhance the thermal properties of PMMA by preparing synthetic polymers possessing another stronger multiple hydrogen bonding moieties on their side chains. The quadruple hydrogen bonding unit 2-ureido-4[1H]-pyrimidinone (UPy) first introduced by Meijer and coworkers[39–41] is a prime example; the rich tautomerism inherent within UPy allows for both self-complementary multiple hydrogen bonding (SCMHB). In addition, UPy exhibits a strong self-association
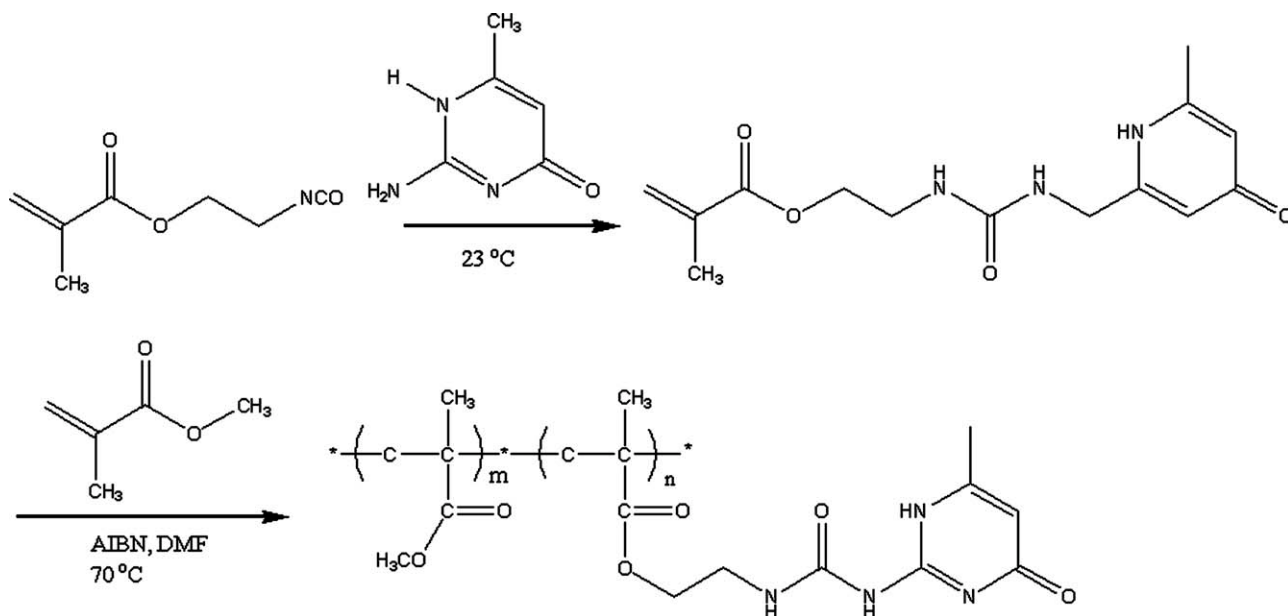
Scheme 1 Synthesis of UPyMA monomer and P(MMA-*co*-UPyMA) copolymers.

equilibrium constant (K_{dim} = 5*10^6 M^{-1}) using a donor-donor-acceptor-acceptor (DDAA) self-complementary array.[42] Long and coworkers[43,44] used free radical polymerization to prepare a series of copolymers based on UPy pendant polymers, poly(butyl acrylate-*co*-UPy-methacrylate) (PBA-*co*-PUPyMA).[43] The glass transition temperatures of PBA-*co*-PUPyMA as the UPyMA content increased. As a result, we chose UPyMA monomer, which was synthesized via a quantitative coupling reaction between 2-isocynatoethyl methacrylate and methyl isocytosine in dimethylsulfoxide (DMSO), for independent copolymerization with methyl methacrylate monomer.[43] In this study, we used differential scanning calorimetry (DSC) to examine the thermal properties of P(MMA-*co*-UPyMA) copolymers featuring SCMHB interactions; in addition, we used Fourier transform infrared (FTIR) spectroscopy, solid state NMR spectroscopy, and viscosity measurements to determine the effects of hydrogen bonding on the domain sizes and molecular motions.

EXPERIMENTAL

Materials

Methyl methacrylate and 2-isocyanatoethyl methacrylate, 6-methylisocytosine (2-amino-4-hydroxy-6-methylpyrimidone: MIS) were purchased from the Aldrich Chemical Company (Milwaukee, USA); they were purified through vacuum distillation and stored under a N$_2$ atmosphere before polymerization. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Dimethylformamide (DMF) and DMSO were distilled from CaH$_2$ under vacuum before use. All other chemicals were of reagent

grade and used as received without further purification. The synthesis of UPyMA monomer prepared through MIS and 2-isocyanatoethyl methacrylate was described previously.[43]

Syntheses of poly(methyl methacrylate-*co*-UPyMA) P(MMA-*co*-UPyMA)

The solution copolymerizations of methyl methacrylate with UPyMA were performed in DMSO at 70°C under an Ar atmosphere within glass reaction flasks equipped with condensers. AIBN was used as the initiator; the mixtures were stirred for ca. 24 h. The products were dissolved in DMSO and then poured into excess MeOH under vigorous agitation to precipitate the copolymers. These copolymers were characterized using ^{1}H-NMR spectroscopy, FTIR spectroscopy, DSC, thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). To determine the reactivity ratios, samples of the copolymers were taken from the reaction flasks during the early stages of copolymerization, i.e., when the degrees of conversion were low (4–9%). Scheme 1 outlines the synthetic procedures and the structures of the various components.

Characterization

Molecular weights and molecular weight distributions were determined at 40°C through GPC using a Waters 510 HPLC equipped with a 410 differential refractometer, a UV detector, and three Ultrastyragel columns (100, 500, and 10^3 Å) connected in series; DMF was the eluent; the flow rate was 0.6 mL min^{-1}. The molecular weight calibration curve was
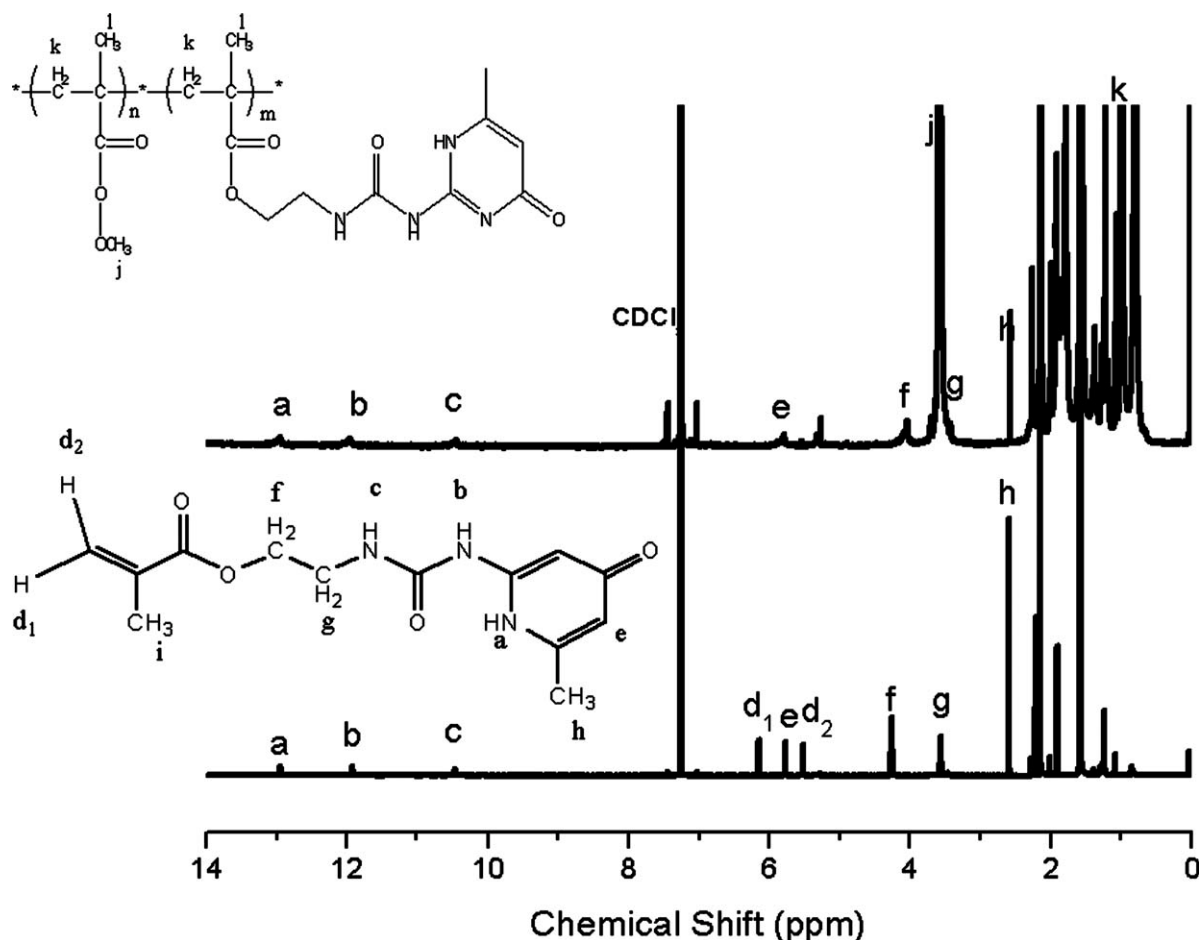
Figure 1 ^{1}H-NMR spectra of UPyMA monomer and U07-PMMA in CDCl$_3$ at room temperature.

obtained using polystyrene (PS) standards. ^{1}H NMR spectra were obtained using an INOVA 500 instrument; CDCl$_3$ was the solvent. The glass transition temperatures of the polymer blend films were determined through DSC using a TA Q-20 instrument. The scan rate was 20°C min^{-1} within the temperature range 30–200°C; the temperature was then held at 200°C for 3 min to ensure complete remove of residual solvent. The values of T_g were measured in the DSC sample cell after the sample (5–10 mg) had been cooled rapidly to 0°C from the melt of the first scan. The glass transition temperature was defined at the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines. FTIR spectra of the polymer blend films were recorded using the conventional KBr disk method. The films used in this study were sufficiently thin to obey the Beer–Lambert law. FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrophotometer; 32 scans were collected at a spectral resolution 1 cm^{-1}. High-resolution solid state ^{13}C NMR spectra were recorded at room temperature using a Bruker DSX-400 spectrometer operated at resonance frequencies of 399.53 and 100.47 MHz for ^{1}H and ^{13}C spectra,

respectively. The ^{13}C cross-polarization (CP)/magic angle spinning (MAS) spectra were measured using a 90° pulse of 3.9 μs, a pulse delay time of 3 s, and an acquisition time of 30 ms; a total of 2048 scans were collected. All NMR spectra were recorded at 300 K using broad-band proton decoupling and a normal cross-polarization pulse sequence. A MAS rate of 5.4 kHz was used for the sample to avoid overlapping of absorptions. The value of $T_{1\rho}$(H) was determined indirectly through carbon atom observation using a 90°-τ-spin-lock pulse sequence before cross polarization. The data acquisition was performed through ^{1}H decoupling with delay times (τ) ranging from 0.1 to 15 ms and a contact time of 1.0 ms. Rheological measurements were performed on an MCR301 controlled stress rheometer (Anton Paar), equipped with Peltier elements for temperature control. All measurements were performed in rotation mode to probe the viscosity of polymer solutions.

RESULTS AND DISCUSSION

UPyMA are soluble in most common solvents. Figure 1 presents ^{1}H-NMR spectra of UPyMA and the

TABLE I
Properties of the PUPyMA-*co*-PMMA Copolymers

Sample	Feed (UPyMA/MMA)	Copolymer[a] (UPyMA/PMMA)	M_w[b]	M_n[b]	PDI[b]	T_g[c] (°C)
Pure PMMA	0 : 100	0 : 100	42,200	31,800	1.63	100
U02-PMMA	1.1 : 98.9	1.9 : 98.1	29,700	19,100	1.56	126
U04-PMMA	1.8 : 98.2	4.1 : 95.9	40,900	25,600	1.59	130
U07-PMMA	3.8 : 96.2	7.4 : 92.6	32,500	18,400	1.76	135

[a] Estimated from ^{1}H-NMR.
[b] Relative molecular weights against polystyrene standard calculated from GPC in THF.
[c] Determined by DSC at 20°C min^{-1}.

P(MMA-*co*-UPyMA) copolymer in CDCl$_3$. For UPyMA monomer, we observe the vinyl group at 5.53 and 6.12 ppm with a relative mole ratio of 1: 1. The N-H signals located at 12.96, 11.93, and 10.47 ppm, are assigned to 4[1H]-pyrimidinone tautomer. The signals of the vinylic hydrogen atoms of UPyMA are absent in the spectrum of U07-PMMA (i.e., the U-PMMA copolymer containing 7 mol % of UPyMA), indicating that the starting monomers had been removed completely. In addition, the N-H signals are remained in U07-PMMA copolymers. We estimated the mole percentage of UPyMA from the ratio of the integrals of the CH$_2$ (H_f = 4.26 ppm) protons of UPyMA and the OCH$_3$ (H_j = 3.55 ppm) protons of MMA. Table I lists the monomer feed ratios and resultant copolymer compositions from which we calculated the reactivity ratios (r_{UPyMA} = 5.33 and r_{MMA} = 0.53) using the methodology of Kelen and Tudos,[45] as discussed previously; these values indicate that these copolymers were essentially random copolymers with a tendency toward blocky structures.

Figure 2 displays DSC curves, recorded at temperatures ranging from 40°C to 160°C, of the P(MMA-*co*-UPyMA) copolymers. Pure PMMA exhibits a single glass tran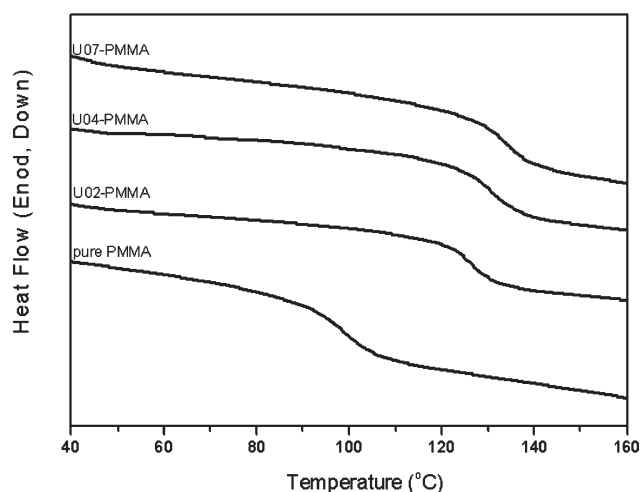sition temperature at ca. 100°C; the glass transition temperatures of the P(MMA-*co*-UPyMA) copolymers increased on increasing their UPyMA contents due to the incorporation of the strongly interacting UPyMA units. The absence of two glass transition temperatures for these copolymers indicates a random copolymerization of these two monomers. Compared with P(MMA-*co*-MAAM) copolymers, the T_g for 8.4-MAAM was 126°C,[10] which was significantly less than T_g for U07-PMMA copolymer (135°C) at a similar molar incorporation of hydrogen bonding sites. This is due to stronger SCMHB interaction (as shown in Scheme 2) in P(MMA-*co*-UPyMA) copolymers than single hydrogen bonding site in P(MMA-*co*-MAAM) copolymers.

Figure 3 shows the TGA curves of pure PMMA and the P(MMA-*co*-UPyMA) copolymers. Thermal degradation of pure PMMA has three distinctive steps. The first is due to decomposition of relatively weak head-to-head linkage. The second is the chain end of PMMA and the third is the PMMA main chains decomposition. The three steps of pure

Figure 2 DSC thermograms of P(MMA-*co*-UPyMA) copolymers.
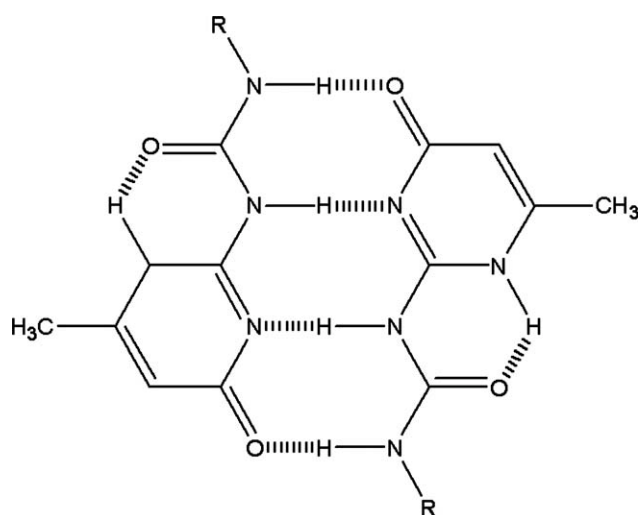
Ka = 5*10^6

R = PMMA-co-UPyMA

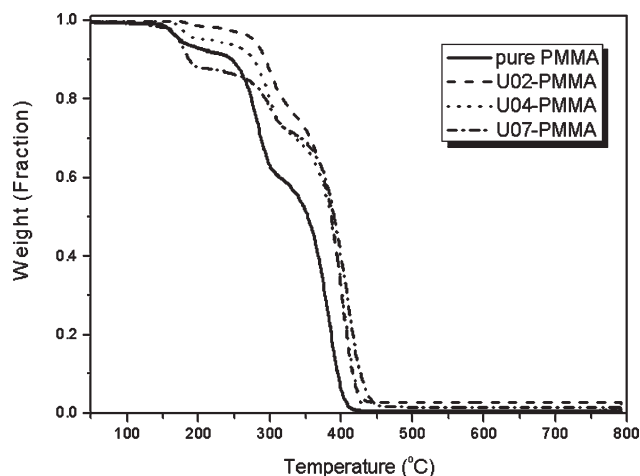**Scheme 2** SCMHB of P(MMA-*co*-UPyMA) copolymers.

Figure 3 TGA thermograms of P(MMA-*co*-UPyMA) copolymers.

PMMA are 167, 270, and 330°C. TGA data indicated that UPyMA containing polymers also appears to be a three-step decomposition reaction, the first degradation step corresponding to the elimination of pendant UPy units. The second and third main chains decomposition temperatures were increased as UPyMA contents increase, and they are higher than pure PMMA about 40°C. It demonstrates that the P(MMA-*co*-UPyMA) copolymer has better thermal stability than that of pure PMMA.

Figure 4 displays FTIR spectra (room temperature) of UPyMA monomer, P(MMA-*co*-UPyMA) copolymers incorporating various UPyMA compositions. The signal of the free C=O groups at 1718 cm^{-1}, hydrogen bonded C=O at 1698 cm^{-1}, free amide I group at 1661 cm^{-1}, hydrogen bonded amide I group at 1644 cm^{-1}, amide II group at 1578 cm^{-1} and 1521 cm^{-1} of pure UPyMA monomer. The free
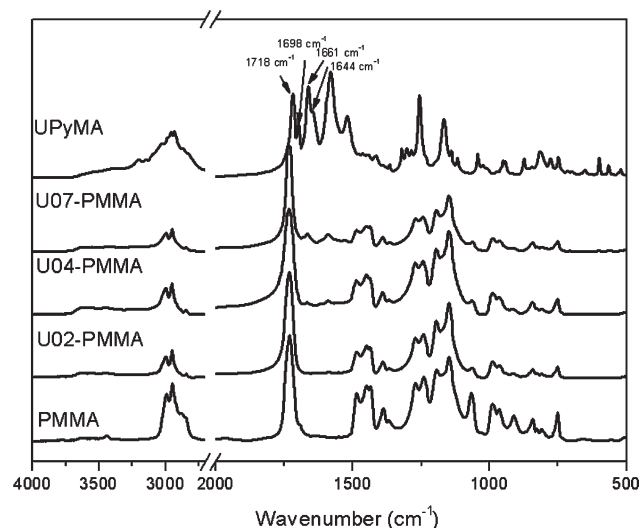
carbonyl C=O group of PMMA is located at 1730 cm^{-1}. Clearly, the corresponding SCMHB UPyMA peaks of P(MMA-*co*-UPyMA) copolymers were increased with the increase of UPyMA contents. However, these self-assembly multiple hydrogen bonding peaks shift to higher wavenumber due to the diluent effect of the PMMA segments.[12] In addition, free carbonyl group at 1730 cm^{-1} of PMMA did not undergo any chemical shifts on increasing the UPyMA contents, indicating that no specific interactions existed between the C=O groups of PMMA and the UPy groups of UPyMA.

Figure 5 presents scale-expanded FTIR spectra of U07-PMMA copolymer recorded at various temperatures. The peaks corresponding to vibration of the free C=O groups of PMMA (1730 cm^{-1}) did not change upon increasing the temperature. In contrast, all of the peaks associated with the SCMHB interactions shifted to higher wavenumber indicating that heat disrupted these noncovalent interactions. At temperatures higher than the value of T_g (> 140°C) of the U07-PMMA, a new peak appeared at ca. 1680 cm^{-1}, corresponding to a free amide I group of UPyMA indicating that the SCMHB interactions of UPyMA had become disrupted.

Evidence for interactions within the copolymers can also be obtained from solid-state NMR spectroscopy, as demonstrated by changes in chemical shifts and/or line shapes.[46] The ^{13}C CP/MAS NMR spectra of pure PMMA, and P(MMA-*co*-UPyMA) copolymers, are shown in Figure 6. Five peaks are observed for pure PMMA, with the peak at δ = 177.9 ppm coming from the carbonyl carbon atom (C-e). UPyMA should have 12 peaks, however only nine peaks were observed in P(MMA-*co*-UPyMA) due to low UPyMA content, and they overlapped with PMMA in copolymer system. Two methylene
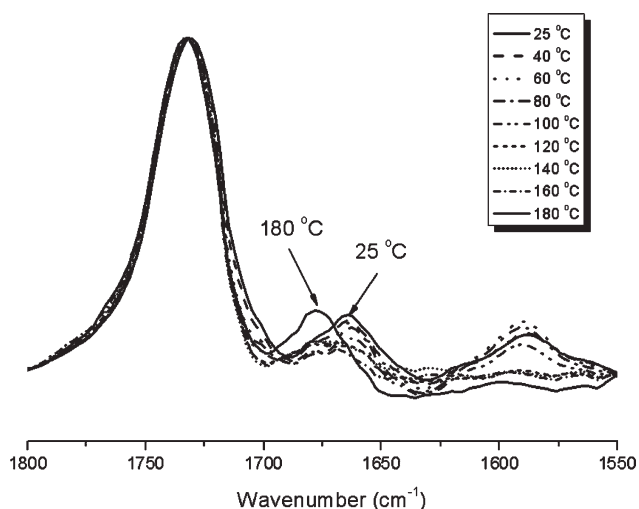

Figure 4 FTIR spectra of UPyMA monomer and P(MMA-*co*-UPyMA) copolymers recorded at room temperature.

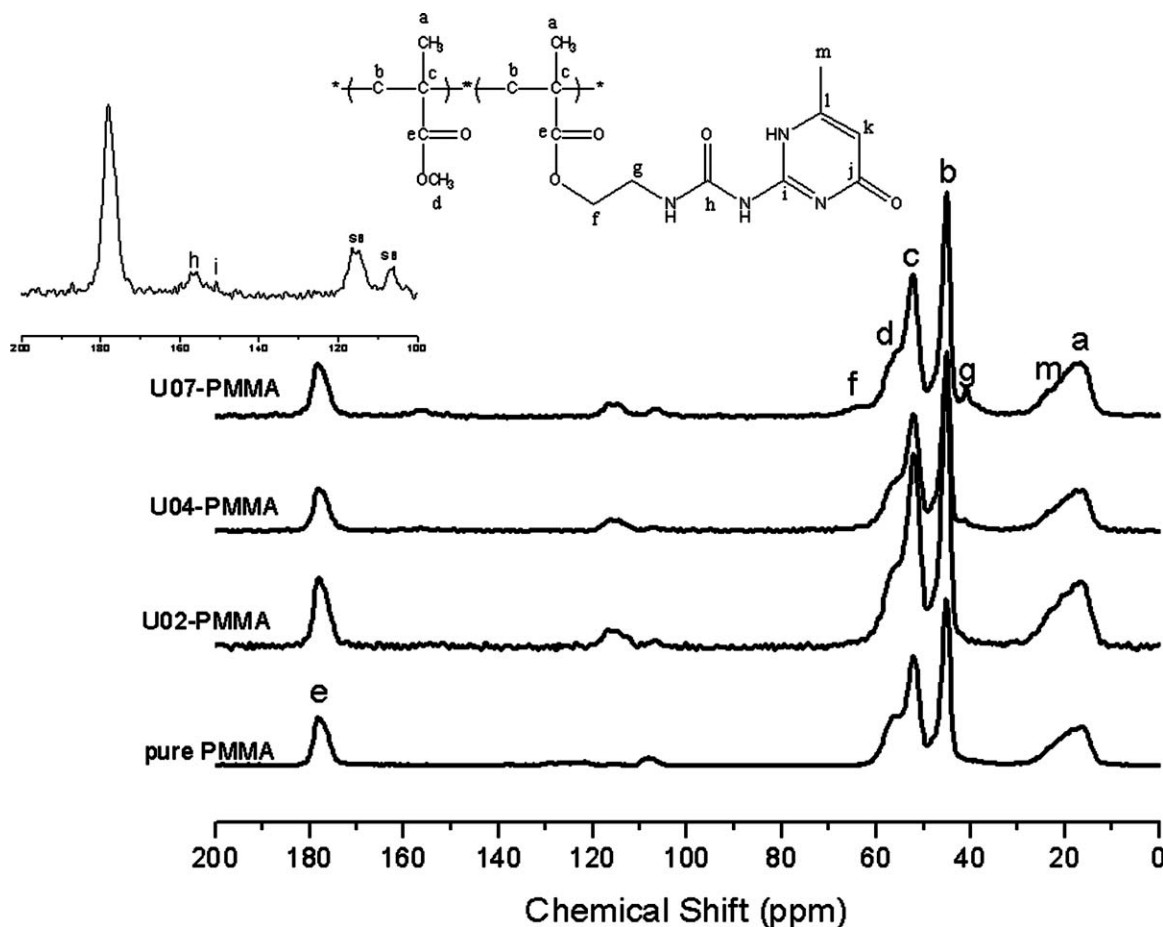**Figure 5** FTIR spectra of U07-PMMA copolymer recorded at various temperatures.

Figure 6 ^{13}C CP/MAS NMR spectral data for P(MMA-*co*-UPyMA) at room temperature.

(CH$_2$) groups, and carbonyl group (C=O) were observed at 41.0 ppm (**C**-g), 63.7 ppm (**C**-f), and 156.1 ppm (**C**-h) with the increase of UPyMA contents in P(MMA-*co*-UPyMA) copolymers. Solid state NMR spectroscopy can also be used to determine the phase behavior and miscibility of blends. A single value of T_g, based on DSC analysis, implies that the mixing of two blend components occurs on a scale of ca. 20–40 nm. The dimension of mixing smaller than 20 nm can be obtained through measurement of the spin–lattice relaxation time in the rotating frame ($T_{1\rho}^H$).[47,48] We measured the values of $T_{1\rho}^H$ of the copolymers through delayed-contact ^{13}C CP/MAS experiments, using the equation $M_\tau = M_o \exp\left[-\tau/T_{1\rho}(H)\right]$, where τ is the delay time used in the experiment and M_τ is the corresponding resonance intensity. Figure 7 presents plots of $\ln(M_\tau/M_0)$ with respect to τ for the signal at 45 ppm of pure PMMA and U04-PMMA. The experimental data are in good agreement with calculated values. The slope of the fitting line provides the value of $T_{1\rho}^H$. We obtained a single composition-dependent value of $T_{1\rho}^H$ for each of pure PMMA and U04-PMMA, suggesting that they are homogeneous on the scale at which the spin-diffusion occurs within

the time $T_{1\rho}^H$. The upper spatial scale of the spin-diffusion path length L can be estimated using the equation $L = (6DT)^{1/2}$, where D (typically 10^{-16} m^2 s^{-1}) is the effective spin-diffusion coefficient depending on the average proton-to-proton distance
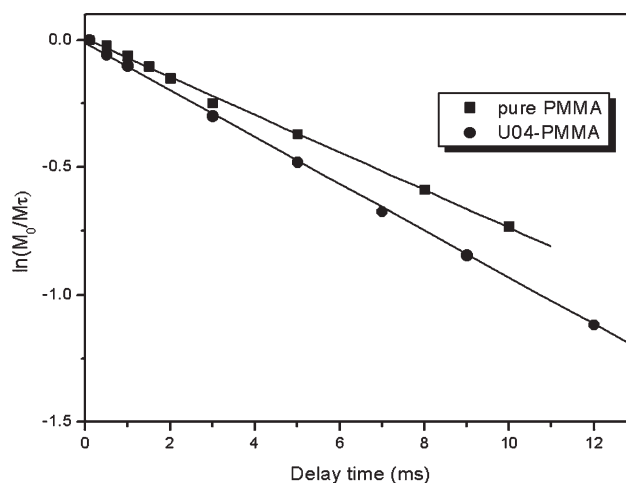

Figure 7 Logarithmic plots of the intensities of 45 ppm for pure PMMA and U04-PMMA with respect to the delay time.

as well as the dipolar interaction. In addition, the value of $T_{1\rho}^H$ for the U04-PMMA was lower than those of pure PMMA. These results imply that the copolymer mixtures featuring multiple hydrogen bonding interactions have relatively smaller domain sizes than pure PMMA. Based on our DSC, solid state NMR spectroscopy, and FTIR spectroscopy analyses, we conclude that the multiple hydrogen bonding interactions in the P(MMA-*co*-UPyMA) led to complex aggregation behavior. We further characterized this copolymer mixture by using an Ubbelohde viscometer to measure the solution viscosity of a mixture of P(MMA-*co*-UPyMA) in chloroform. The formation of supramolecular polymers in the P(MMA-*co*-UPyMA) provided a higher solution viscosity relative to that of pure PMMA as shown in Figure 8; in addition, the viscosity increased upon increasing the concentrations of the copolymers. Similarly, Figure 9 shows the zero shear viscosity of the U07-PMMA sample were determined from extrapolation to the y-axis, which was significantly higher than pure PMMA with the same concentration (10 wt % in THF solution). The increase viscosity was attributed to the formation of intermolecular complementary hydrogen bonds and supramolecular structure for U07-PMMA copolymer.

CONCLUSIONS

We have used free radical polymerization to synthesize UPy-functionalized PMMA random copolymers. Incorporating SCMHB units into PMMA enhanced the thermal properties and dramatically increased the viscosity as a result of the formation of supramolecular polymers. FTIR and solid-state NMR spectroscopic analyses both provided positive evidence for hydrogen bonding interactions within these copoly-
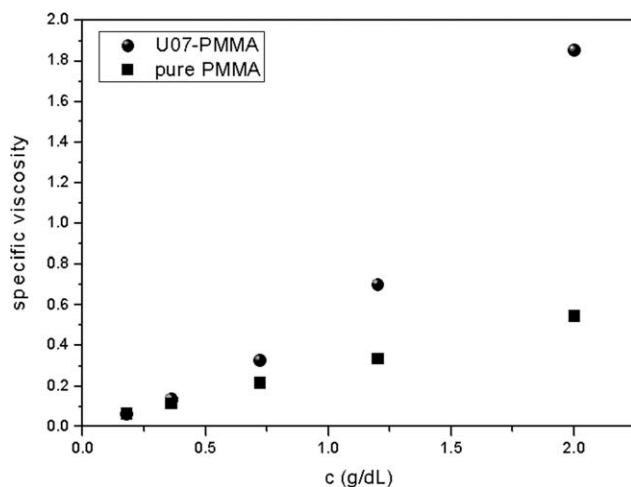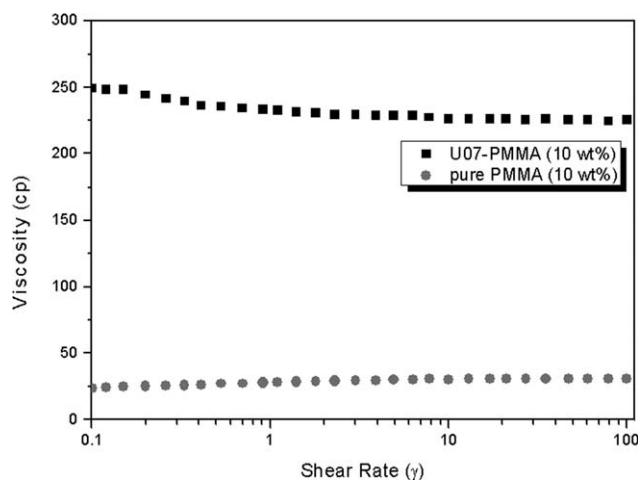
Figure 9 Solution viscosities of pure PMMA and U07-PMMA in THF solution.

mer systems. We obtained a single value of the spin-lattice relaxation times in the rotating frame for the copolymer that was lower than those of the pure PMMA, suggesting a relative lower domain size in P(MMA-*co*-UPyMA) copolymers. Thus, significant increases in the value of T_g of PMMA can be achieved through copolymerization of methyl methacrylate individually with SCMHB monomers.

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Figure 8 Plots of specific viscosity of U07-PMMA and pure PMMA in THF solution with respect to concentration.

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