Synthesis and Characterization of Poly[4-(2-Thiazolylazo)Phenyl Methacrylate]-Co-Poly(Methyl Methacrylate)

Rui Zhang, Jun Yang, Weilin Sun, Zhiquan Shen

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 2 December 2005; accepted 20 April 2006
DOI 10.1002/app.25041

ABSTRACT: A new methacrylic monomer, 4-(2-thiazolylazo)phenylmethacrylate (TPMA) was synthesized. Copolymerization of the monomer with methyl methacrylate (MMA) was carried out by free radical polymerization in THF solution at 70 ± 0.5°C, using azobisisobutyronitrile (AIBN) as an initiator. The monomer TPMA and the copolymer poly(TPMA-co-MMA) were characterized by Fourier transform infrared (FTIR), ^{1}H nuclear magnetic resonance (NMR), and elemental analysis methods. The polydispersity index of the copolymer was determined using gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) of the copolymer performed in nitrogen revealed that the copolymer was stable to 270°C. The glass transition temperature (T_g) of the copolymer was higher than that of PMMA. The copolymer with a pendent aromatic heterocyclic group can be dissolved in common organic solvents and shows a good film-forming ability. Both the monomer TPMA and the copolymer poly (TPMA-co-MMA) have bright colors: orange and yellow, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2152–2157, 2007

Key words: 4-(2-thiazolylazo)phenyl methacrylate; copolymer; methyl methacrylate; synthesis

INTRODUCTION

For several decades, various aromatic heterocyclic polymers have been studied for applications in aviation, electronics, chemical engineering, and mechanical engineering, and so on. They are not only used as structural materials owing to their good mechanical properties, thermal stability, radioresistance, and anticorrosion, but have served as functional materials in recent years, such as heat-resistant and gas-separating film,[1] conductors,[2] and optoelectronic and magnetic materials.[3–8] Meanwhile, the importance of acrylic polymers both in industrial applications[9–11] and basic research fields such as magnetic, optical and liquid crystal materials[12–14] has long been recognized. The present work synthesized a new methacrylate containing aromatic heterocycle, which was then copolymerized with methyl methacrylate (Scheme 1), extending the study of aromatic heterocyclic methacrylate.

EXPERIMENTAL

Materials

2-Aminothiazole was purchased from MERCK-Schuchardt (Hohenbrunn, Germany), used without further purification. MMA was washed in 5% sodium hydroxide aqueous solution and deionized water successively, then dried with anhydrous magnesium sulfate for 24 h, and distilled under reduced pressure. Dimethylsulfoxide (DMSO) and triethylamine (TEA) were dried with calcium hydride and distilled. Tetrahydrofuran (THF) was dried over sodium/benzophenone and was distilled just before use. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and dried in vacuo. All other reagents were used as received.

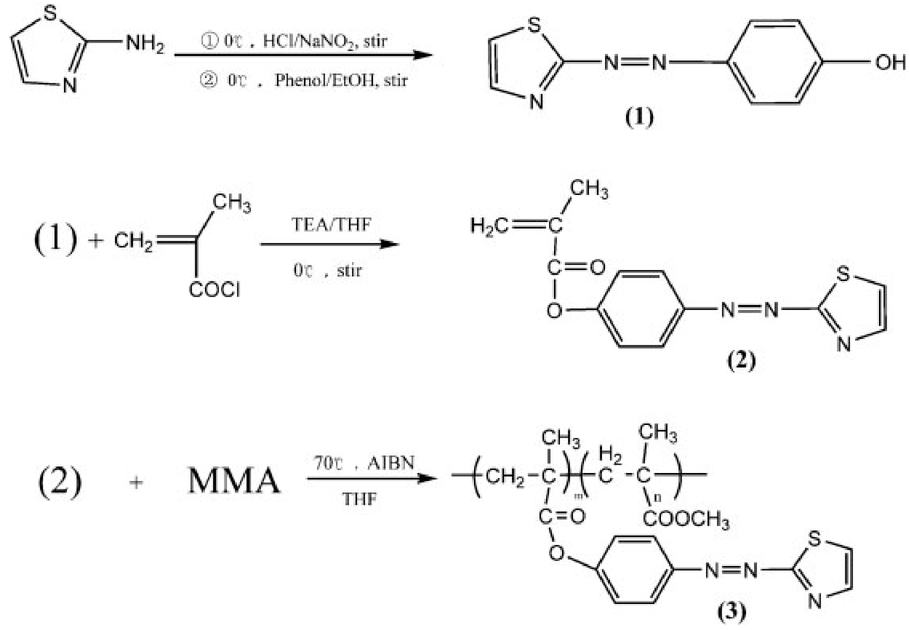
Synthesis of the monomer and polymer

4-(2-thiazolylazo)phenol (TAP) was prepared according to the method described by Tensen.[15] Thus, 2-aminothiazole (5.0 g, 50 mmol) was dissolved in 3.6 mol/L sulfuric acid (50 mL), and the solution was cooled in an ice bath to 0°C. To this was slowly added a cold solution of sodium nitrite (3.5 g, 50 mmol) in deionized water (25 mL) with vigorous stirring. The resulting solution was then slowly added to a stirring solution of phenol (4.7 g, 50 mmol) in

---

Correspondence to: W. Sun (opl_sunwl@zju.edu.cn).
Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 20374044, 20434020.

Journal of Applied Polymer Science, Vol. 103, 2152–2157 (2007)



Scheme 1 Synthesis of TAP, TPMA, and poly(TPMA-co-MMA).

absolute ethanol at 0°C. The red precipitate, which was formed in 1 h, was filtered and washed with a mount of deionized water until the washing water exhibits to neutral, then recrystallized by boiling in refluxing ethanol with activated carbon, filtrated through a hot filtration funnel. The resulting red sheet-like crystal was dried in vacuo. The yield is 6.8 g (66%).

TAP

IR (KBr, cm^{-1}): 2500–3400 (broad, OH), 1605, 1584 (conjugated aromatic rings), 1248 (C—O), 635 (C—S); ^{1}H NMR (δ, ppm) (DMSO-d): 10.73 (1H, —OH), 6.94–6.99, 7.79–7.83 (4H, benzyl H), 7.86, 8.00–8.03 (2H, thiazolyl H). Melting point: 217.5–218.1°C.

4-(2-thiazolylazo)phenyl methacrylate (TPMA) was prepared from TAP and methacryloyl chloride. Methacryloyl chloride was synthesized from methacrylic acid and thionyl chloride using the procedure of No et al.[16] TAP (3.08 g, 15 mmol) and TEA (2.25 mL, 18 mmol) were dissolved in 100 mL of THF and were placed in a dry one-neck round-bottom flask fitted with a magnetic stirrer and a dropping funnel. The reaction mixture was cooled to 0°C, then stirred in an ice bath at 0–5°C. Methacryloyl chloride (1.75 mL, 18 mmol) dissolved in 20 mL of THF was added dropwise through the dropping funnel in 1 h. After the addition, the reaction mixture was stirred for 4 h at 0°C and left overnight at 2°C to complete the reaction. The precipitated triethylammonium chloride was filtered off, and the solvent in the filtrate was distilled under reduced pressure at 40°C. The residue obtained was dissolved in ether and washed three times with 0.1% solution of sodium hydroxide and then with deionized water several times to remove the sodium hydroxide. The ether solution was dried using unhydrous magnesium sulfate, and the solvent was distilled under reduced pressure. The orange product was dried under vacuum at 60°C for 24 h. The yield is 3.2 g (78%).

TPMA

IR (KBr, cm^{-1}): 3078, 3107 (aromatic and double bond H), 2930, 2964 (CH_3), 1730 (C=O), 1636 (C=C), 1589, 1581 (aromatic ring), 1247, 1138 (C—O—C), 630 (C—S). ^{1}H NMR (δ, ppm)($CDCl_3$-d): 7.30–7.44 (3H, benzyl H), 8.04–8.09 (3H, 1 H of benzyl ring, and 2 H of thiazole ring), 6.39, 5.81 (2H, CH_2), 2.08 (3H, CH_3). Elemental analysis (%): calc: C = 57.10, H = 4.06, N = 15.38; Found: C = 57.00, H = 4.16, N = 14.57; Melting point: 92–94°C.

Free radical polymerization of TPMA was attempted with AIBN or benzoyl peroxide as the initiator in dried and degassed THF or toluene. The reaction mixture under nitrogen was tightly sealed and heated at 70°C for 24 h. No polymer was formed, and the starting material was recovered unchanged. Hot polymerization of TPMA in dried and degassed DMSO heated at 120°C for 24 h was also attempted. Again, no polymer was formed, maybe due to the inhibitory effect of TPMA. Indeed, similar phenomenon has been reported before.[17,18]

In a dried and degassed ampule, TPMA (1.092 g, 4 mmol), and AIBN (0.0394 g, 0.24 mmol) were input, degassed, and flushed with nitrogen three times, and were then sealed tightly; 20 mL newly distilled THF was injected into it with a syringe. Finally when the

TABLE I
Copolymer Composition and Molecular Weight and Polydispersity (PD) Data

Polymer	m_1[a]	M_1[a]	[η][b] [dL/g]	*M*n (g/mol)	*M*w (g/mol)	PD	C
Poly(TPMA-co-MMA)	0.167	0.222	0.411	5448	9167	1.675	0.363

[a] Where m_1 is the feed ratio of TPMA, and M_1 is the mole fraction of TPMA in the copolymer.
[b] Measured at 30°C, in acetone.

solution was well proportioned, methyl methacrylate (2.0 g, 20 mmol) was injected in. The ampule was heated at 70 ± 0.5°C for 24 h. The reaction mixture was then precipitated in a large volume of petroleum ether. The product was redissolved in chloroform and then reprecipitated in petroleum ether for several times. The resulted copolymer was dried under vacuum at 60°C. The average molecular weight and dispersity of the copolymer were determined using gel permeation chromatography (GPC) (see Fig. 6 and Table I).

Poly(TPMA-co-MMA)

IR (KBr, cm^{-1}): 3106, 3084 (aromatic H), 2930, 2964 (CH_3), 1727, 1756 (C=O), 1589, 842 (aromatic ring), 1202, 1145 (C—O—C), 630 (C—S). ^1H NMR (δ, ppm) ($CDCl_3$-d): 7.2–8.2 (aromatic H), 3.5–3.7 (O—CH_3), 0–2.3 (H of the main chain and C—CH_3). Elemental analysis (%): calc: C = 58.74, H = 6.26, N = 6.73, found: C = 58.14, H = 6.16, N = 7.22. Intrinsic viscosity [η] = 0.41 dL/g (acetone, 30°C).

Measurements

IR spectra were recorded with a Bruker Vector 22 spectrometer. ^1H NMR spectra were recorded on a Bruker Advance AMX-500 NMR instrument with tetramethylsilane (TMS) as internal standard. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6 instrument. The differential scanning calorimetric (DSC) curve of the copolymer was recorded on a Perkin-Elmer Pyris 1 by maintaining the heating rate at 10°C/min in nitrogen atmosphere. Elemental analysis was measured through a Thermo Finnigen Flash EA 1112 instrument. GPC was performed using the Waters GPC with 2410 RI detector.

RESULTS AND DISCUSSION

Solubility

In this study, 20 mg of the copolymers was mixed with 2 mL different solvents in respective test tubes. After setting aside the closed tubes for 24 h, the solubility was observed. The copolymer is soluble in chloroform, acetone, dimethyl formamide, DMSO, tetrahydrofuran, toluene, xylene, and insoluble in *n*-hexane, petroleum ether, and methanol.

Infrared spectra

Figure 1 shows the IR spectrum of TAP. Figure 2 shows the IR spectra of the monomer (TPMA) and the copolymer. In Figure 1, the strong absorptions from 2500 to 3500 cm^{-1} are attributed to the associated O—H vibration. The ring stretching vibrations of the conjugated thiazole and benzene rings were observed at 1605, 1584, 1507, 1466, and 1433 cm^{-1}, respectively.

Figure 2 shows the IR spectra of TPMA, the monomer (a) and poly(TPMA-co-MMA), the copolymer (b). In curve (a), the peaks at 2930, 2984 cm^{-1} were assigned to the stretching vibration of the aliphatic C—H, the peak at 1733 cm^{-1} was attributed to the stretching vibration of C=O ester group, the peak at 1636 cm^{-1} was due to aliphatic C=C stretching vibration, peaks at 1600, 1581 cm^{-1} are related to the aromatic ring stretching vibrations, peaks at 1050–1231 cm^{-1} are assigned to the stretching vibrations of aromatic C—O group. In curve (b), it can be seen that the sharp peak at 1636 cm^{-1} disappears, indicating that upon polymerization the aliphatic C=C bond disappears. The stretching of the double bond in the carbonyl group attached to the aromatic ring through —O— is shifted

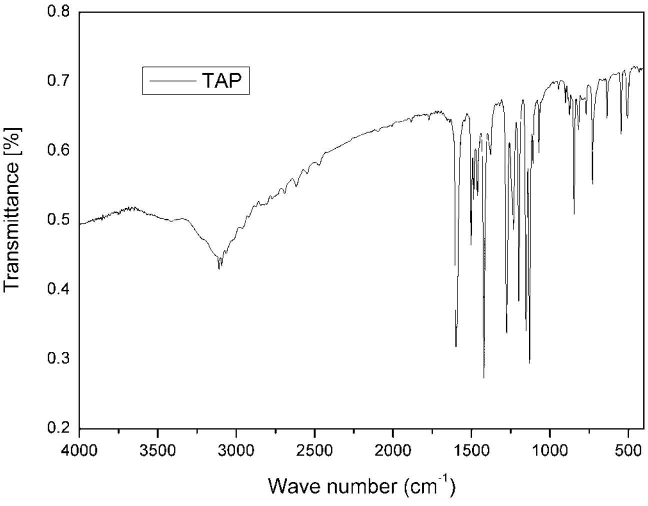


Figure 1 IR spectrum of TAP.

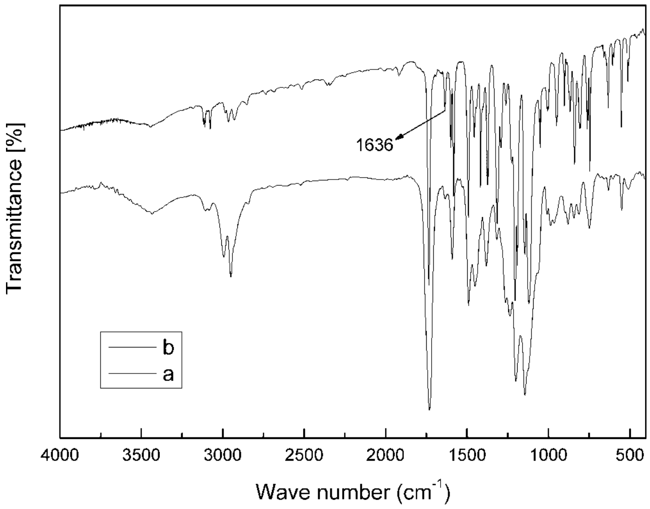


Figure 2 IR spectra of (a) TPMA, and (b) poly(TPMA-co-MMA).

to larger wavenumber (1756 cm^{-1}) compared with the value for the carbonyl group (1730 cm^{-1}) in the monomer due to loss of conjugation after polymerization.

^{1}H NMR spectra

The ^{1}H NMR spectra Figures 3 and 4 show the chemical shifts of TAP and TPMA, respectively. Comparing with that of TAP, the chemical shifts of aromatic protons in TPMA are shifting slightly to up field. The chemical shifts at 5.81 and 6.39 ppm are signals of protons attached with the aliphatic double bond. The resonance signal at 2.08 ppm is related to the methyl group. The proton signal at 10.73 ppm in TAP attributed to the hydroxyl group disappears in TPMA. In Figure 5, the proton signals of the aryl group in the copolymer can be seen between 7.26 and 8.05 ppm. The signals at between 3.5 and 3.8 ppm are due to methoxyl group of MMA. The broad signals at 0.85–2.2 ppm are attributed to the methylene group of the backbone and the methyl group attached to the backbone.

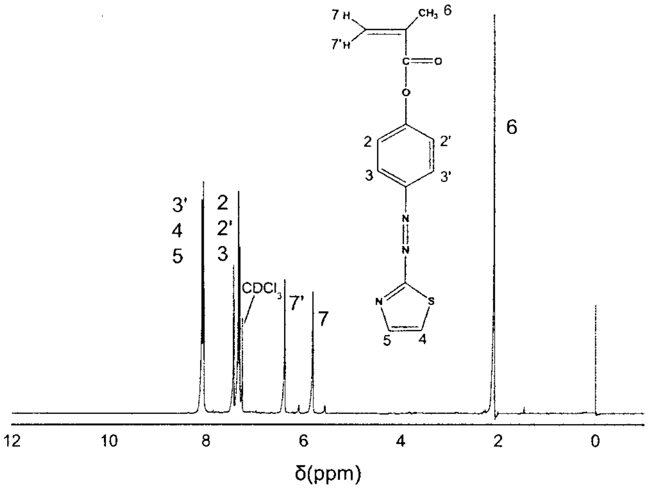


Figure 4 ^{1}H NMR spectrum of TPMA.

Molecular weights

The number-average, weight-average molecular weights, and polydispersity of the copolymer were determined by gel permeation chromatography (see Figure 6). The M_w/M_n value of the copolymer shows no general trend of termination.

Glass transition temperature

The DSC thermogram of the resultant copolymer is shown in Figure 7. A single glass transition temperature (T_g) is clearly presented at 133°C,which is much higher than that of PMMA homopolymer (105°C, atactic[19]). It is believed that the large rigid thiazoylazo phenyl group

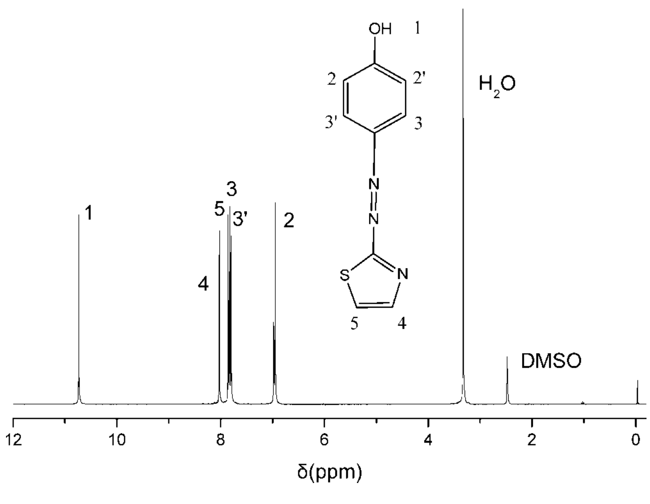


Figure 3 ^{1}H NMR spectrum of TAP.

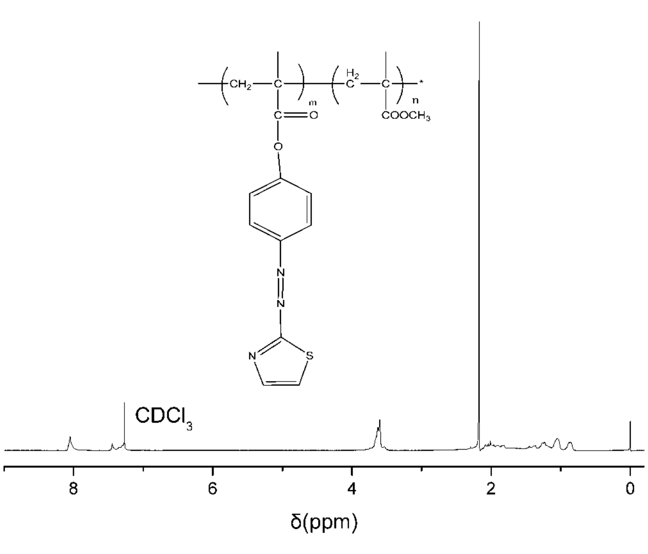


Figure 5 ^{1}H NMR spectrum of poly(TPMA-co-MMA).

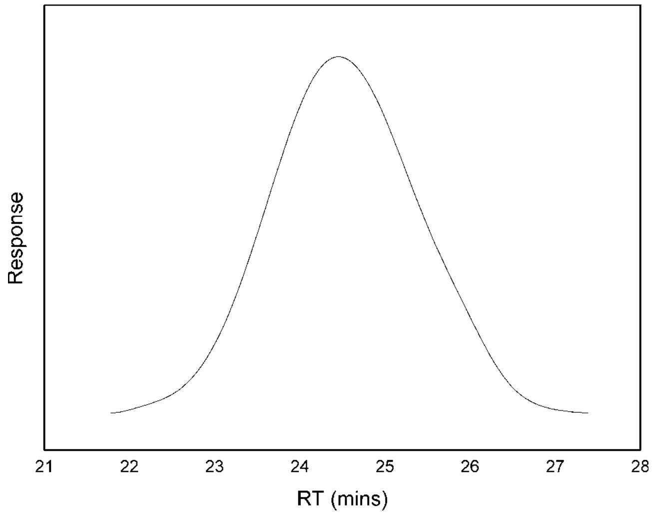


Figure 6 GPC curve of poly(TPMA-co-MMA).

contributes mainly to the increase of the T_g of the copolymer. Combining with the GPC result, one single T_g in DSC curve implies that no homopolymer corresponding to PMMA or PTPMA is included in the copolymer.

Thermal analysis

The thermal stability of the copolymer was studied by TGA under nitrogen atmosphere at the heating rate of 10°C/min. The result shown in Figure 8 indicates that the decomposition of the copolymer poly(TPMA-co-MMA) starts at about 270°C. The weight loss of the copolymer is 30% when the temperature reaches 380°C. In contrast, the decomposed percentage of the PMMA homopolymer is as high as 75%[20] at 380°C, although PMMA also begins to decompose at about 270°C. Therefore, introducing the thermal stable aromatic heterocycle moiety into the molecular structure apparently improves the heat resistance of the MMA copolymer.

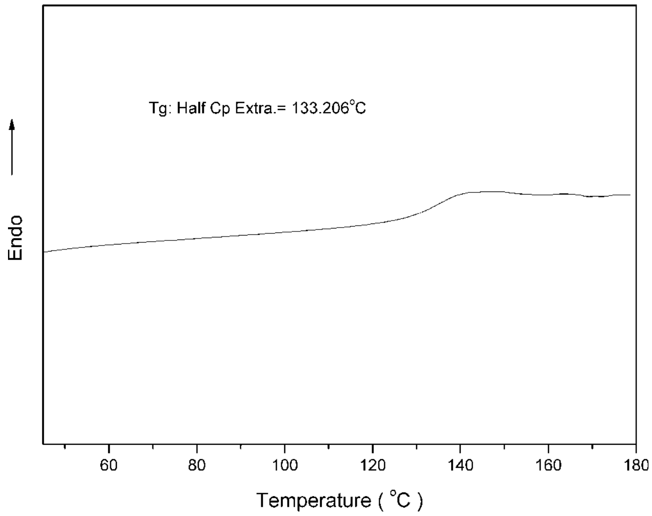


Figure 7 DSC curve obtained on the second heating of poly(TPMA-co-MMA).

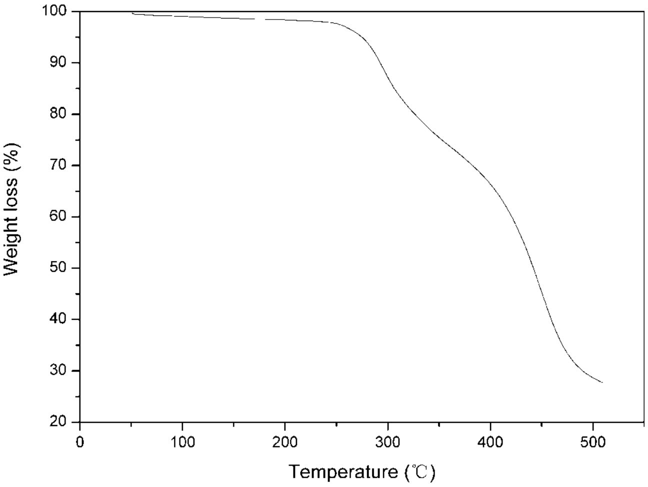


Figure 8 TGA curve of poly(TPMA-co-MMA).

Copolymer composition

The chemical structure of copolymer may be represented as (3) in Scheme 1. The average composition of the copolymer sample was determined from the ^1H NMR spectrum. The assignment of the resonance peaks in the ^1H NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains.

Thus, the mole fraction of TPMA in the copolymer chain was calculated from measuring the integrated peak areas of aromatic protons of the TPMA unit and —OCH_3 protons of the MMA unit.

The following expression is used to determine the composition of the copolymer. Let m_1 be the mole fraction of TPMA and 1-m_1 is that of MMA. TPMA contains 6 aromatic protons and —OCH_3 of MMA contains three protons:

$$\mathrm{C} = \frac{\text{Integrated peak area of aromatic protons } (I_{\mathrm{Ar}})}{\text{Integrated peak area of —OCH}_3\text{ protons} + I_{\mathrm{Ar}}} = \frac{6m_1}{6m_1 + 3(1 - m_1)} \quad (1)$$

This on simplification gives

$$m_1 = \frac{C}{2 - C} \quad (2)$$

From eq. (2), the mole fraction of TMPA in the copolymer was determined by measuring the integrated peak area of aromatic and —OCH_3 proton signals. The value of C and the mole fraction of TPMA in the copolymer are shown in Table I.

CONCLUSION

TPMA was prepared by reacting TAP dissolved in THF with methacrylol chloride in the present of triethylamine, and was characterized with IR, NMR, and EA. The copolymer, poly(TPMA-co-MMA), was prepared and determined with IR, NMR, EA methods. The results were in good agreement with each other. The GPC result of the copolymer indicates that molecular weights data follow a normal distribution and has a narrow polydispersity. The TGA and DSC curves of the copolymer show an increase in the initial decomposition temperature and a higher T_g compared with that of PMMA. Both the monomer TPMA and the copolymer poly(TPMA-co-MMA) have bright colors, orange and yellow, respectively.

References

1. Sun, W. L.; Gao, X. S.; Lu, F. C. J Appl Polym Sci 1997, 64, 2309.
2. McClain, M. D.; Dudis, D. S. Synth Met 2001, 116, 199.
3. Ogata, N. Pure Appl Chem 1991, 63, 951.
4. Weng, J.; Sun, W. L.; Jiang, L. M.; Shen, Z. Q. Macromol Rapid Commun 2000, 21, 1099.
5. Weng, J.; Sun, W. L.; Jiang, L. M.; Shen, Z. Q. J Appl Polym Sci 2001, 81, 1353.
6. Liu, J. G.; Sun, W. L.; Lu, F. C. J Appl Polym Sci 2000, 82, 818.
7. Weng, J.; Jiang, L. M.; Sun, W. L.; Shen, Z. Q.; Liang, S. Q. Polymer 2001, 42, 5491.
8. Jiang, L. M.; Sun, W. L.; Weng, J.; Shen, Z. Q. Polymer 2002, 43, 1563.
9. Selvamalar, C. S.; Krithiga, T.; Penlidis, A.; Nanjundan, S. React Funct Polym 2003, 56, 89.
10. Ito, C. K.; Jung, J. H. J Polym Sci Part A Polym Chem 2002, 40, 1200.
11. Warson, H. In The Application of Synthetic Resin Emulsion; Ernest Benn: London, 1972; p 38.
12. Wulff, G.; Dhal, P. K. Macromolecules 1990, 23, 4525.
13. Genin, H.; Hoffmann, R. Macromolecules 1998, 31, 444.
14. Zheng, P.; Jiang, L. M.; Sun, W. L.; Shen, Z. Q. J Appl Polym Sci 2005, 98, 83.
15. Tensen, B. S. Acta Chem Scand 1960, 14, 927.
16. No, V. B.; Kristsova, S. N.; Petrva, N. E.; Mazalova, Z. I.; Sorokin, V. V.; Tryukhan, A. N.; Sokolov, V. V. U. S. Pat. 1595835 (1991).
17. Kaplan, M. L.; Haddon, R. C.; Feit, E. D. J Org Chem 1978, 43, 4642.
18. Pittman, C. U., Jr.; Ueda, M.; Liang, Y. F. J Org Chem 1979, 44, 3639.
19. Brundrup, J.; Immergut E. H. Polymer Handbook; 3rd ed.; Wiley: New York, 1989; Vol I; p 219.
20. Thamizharasi, S.; Gnanasundaram, P.; Reddy, B. S. R. Eur Polym J 1997, 33, 1487.