

Synthesis of Acetophenone Formaldehyde Resin Containing ABA Type Block Copolymers by ATRP

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Received 10 July 2008; accepted 7 March 2010

DOI 10.1002/app.32394

Published online 21 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Well-defined ABA type block copolymers of acetophenone formaldehyde resin (AFR) and methyl methacrylate (MMA) were synthesized via atom transfer radical polymerization. In the first step, acetophenone formaldehyde resin containing hydroxyl groups was modified with 2-bromopropionyl bromide. Resulting difunctional macroinitiator was used in the ATRP of MMA using copper bromide (CuBr)/*N,N,N',N'',N'''*-pentamethyl-diethylenetriamine (PMDETA) as the catalyst system at 90°C. The chemical composition and structure of the copolymers were characterized by nuclear magnetic resonance (¹H-NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and molecular weight measurement. Gel permeation chromatography (GPC) was used to study the molecular weight distributions of the AFR block copolymers. M_n up to 24,000 associated with

narrow molecular weight distributions (PDI < 1.5) were obtained with conversions up to 79%. Coating properties of obtained block copolymers such as adhesion and reflectance values were investigated. They showed good adhesion properties on Plexiglass substrates. Reflectance values increased as the resin content of polymer increased. The thermal properties of all polymers were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All block copolymers showed higher thermal stability than their precursor AFR resin. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 183–189, 2011

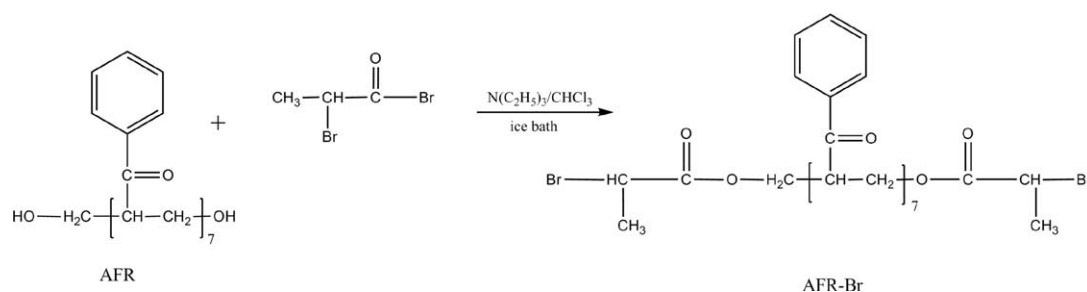
Key words: acetophenone formaldehyde resin; block copolymer; atom transfer radical polymerization; poly(methylmethacrylate)

INTRODUCTION

The modification of acetophenone formaldehyde resins leads to products which show distinct differences in relation to the customary ketone and aldehyde resins, thereby opening up new applications. The reaction of hydroxyl groups, which form from the ketone groups in the course of hydrogenation, with aliphatic diisocyanates leads to high-grade specialty binders.^{1–3} Acetophenone formaldehyde resins are used as cost-effective binders in coating materials and printing inks, in combination with other raw materials such as cellulose nitrate. They improve gloss, fullness, hiding power, solids content, adhesion, and drying. Copolymers of ketonic resins have been the subject of recent research because the ketonic resin segments improve adhesive, solubility, gloss, and light stability of parent polymers.^{4,5} These copolymers have been synthesized via condensation polymerization, free radical polymerization, redox polymerization, and promoted cationic polymerization routes.^{6–14} The control of the molar mass characteristics and monomer sequence in block copolymers are becoming increasingly impor-

tant in macromolecular engineering.^{15,16} The classical living anionic or cationic polymerization techniques have been applied to the synthesis of copolymers with controlled characteristics.^{17,18} However, neither technique can be applied to monomers containing a variety of functional groups, at least in principle, should be of great practical importance because it starts from well-known resins able to undergo condensation polymerization, and allows the design of radical polymerization is definitely less sensitive to experimental conditions purity, reaction novel materials with highly differentiated structures and architectures. Recently, significant progress has been made in the field of living free radical polymerization (FRP), such as nitroxide-mediated stable FRP, atom transfer radical polymerization (ATRP), reverse ATRP, and reversible addition-fragmentation chain transfer.^{19,20} Among them, ATRP has been successfully applied to the synthesis of well-defined macromolecular architectures such as comb, star, branched, and dendritic macromolecules.^{21–28,45} ATRP has been shown to be a versatile technique for the controlled polymerization of many monomer classes, including (meth)acrylates, (meth)acrylamides, (substituted) styrenes, and miscellaneous monomers.^{29–39,46–47} Moreover, this CRP technique is tolerant to a wide range of functional monomers, solvents, and initiators.

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Scheme 1 Synthesis of AFRBr.

Poly(methyl methacrylate) (PMMA), as a kind of transparent polymeric material, has many excellent properties, including colorlessness, high light transmittance, chemical resistance, and weathering corrosion resistance.⁴⁰ PMMA is widely used for several applications, such as automobile parts, sign boards, carports, compact disks, lenses, and optical fibers.^{41,42} Beside this, there is no literature study related to ketonic resin—MMA copolymers.

As part of a project to exploit controlled radical polymerization in preparing new materials with highly controlled characteristics, the present work concerns the preparation of functional triblock (PMMA-*b*-AFR-*b*-PMMA) copolymers containing ketonic resin groups. Block copolymers were prepared through the polymerizations of acetophenone formaldehyde resin (AFR) and methyl methacrylate (MMA) to give triblock copolymer.

After functionalization of the AFR resin, it is used as a macroinitiator for MMA polymerization. For this purpose, bromide functional, AFRBr was synthesized by esterification of AFR with 2-bromopropionyl bromide.

EXPERIMENTAL

Tetrahydrofuran (J.T. Baker) was dried over potassium hydroxide and distilled over CaH_2 . Dimethyl sulfoxide (Merck) was refluxed over CaH_2 and distilled under reduced pressure (76°C and 12 mmHg). Chloroform (J.T. Baker) was shaken with several portions of concentrated H_2SO_4 , washed thoroughly with water, and dried with CaCl_2 before being filtered and distilled (61°C and 760 mmHg). MMA (Fluka) was purified by conventional methods and distilled in vacuum over CaH_2 just before use. Other chemicals, *N,N,N',N'',N''*-pentamethyl-diethylenetriamine (PMDETA) (97% Aldrich), acryloyl chloride (99% Aldrich), copper(I)bromide (98%, Aldrich), anisole (99% Acros), triethylamine (99% Acros), 2-bromopropionyl bromide (97% Aldrich), acetophenone (99% Merck), and formaldehyde (Fluka, 37% solution) were used without further purification.

Analysis

FT-IR spectra was measured using model recorded Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. ¹H-NMR spectra were measured on a Bruker AC (250 MHz, Darmstadt, Germany) spectrometer by using $\text{DMSO}-d_6$ or CDCl_3 as a solvent and tetramethylsilane as the internal standard. Block copolymer composition and molecular weight from NMR was determined by the ratio of the signal intensity of aromatic protons peak region so that of methoxy peak region. Gel permeation chromatography (GPC) analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector and three Agilent Zorbax PSM 1000S, 300S, and 60S columns (6.2×250 mm, 5 micron) measuring in the range of 10^4 to 10^6 , 3×10^3 to 3×10^5 , 5×10^2 to 10^4 , respectively. THF was used as the eluent at a flow rate of 0.5 mL/min at 30°C. The molecular weights (M_w s) of the polymers were calculated with the aid of polystyrene and PMMA standards. The thermal properties of the copolymers were measured by differential scanning calorimeters (TA, DSC Q10) in a flowing nitrogen atmosphere from 30°C at scanning rate of 10°C/min. Thermal stability of copolymers was measured by

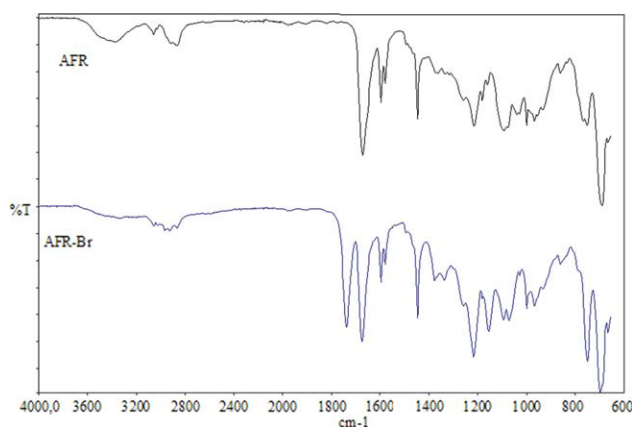
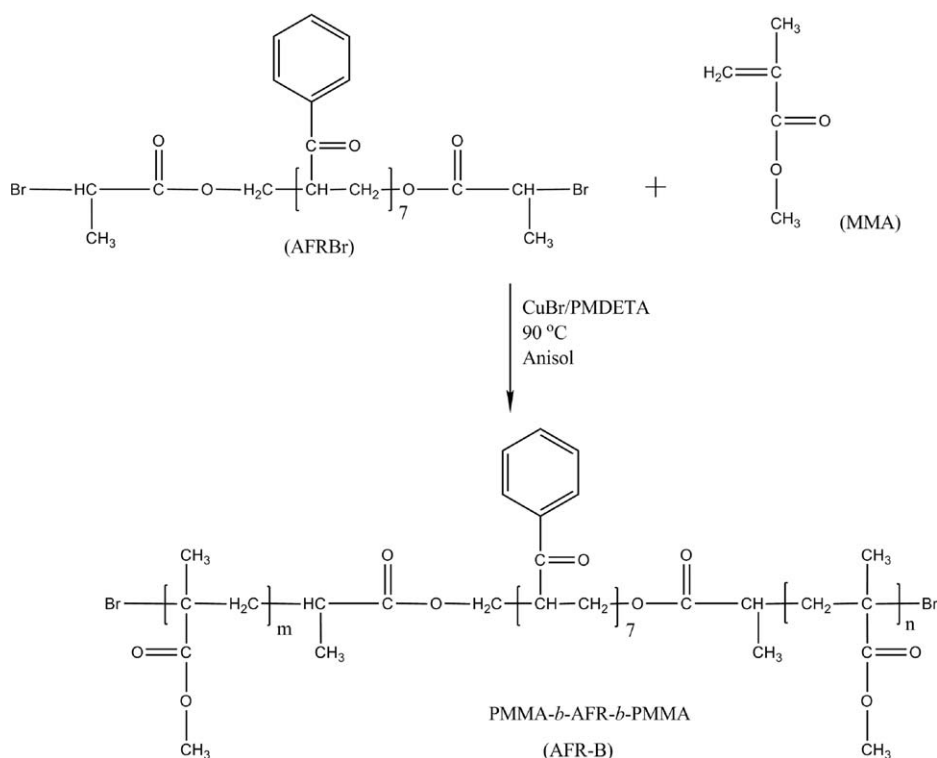


Figure 1 FT-IR spectrum of AFR resin and AFRBr macroinitiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2 Synthesis of triblock PMMA-*b*-AFR-*b*-PMMA copolymer (AFR-B).

thermo gravimetric analysis (TA, TGA Q50) in a flowing nitrogen atmosphere at heating rate of 20°C/min. Copolymer resin films were prepared by using SCS Spincoater P6700 instrument. Spectrophotometric reflectance analysis of copolymer films was performed with Scinco (S-3100) instrument. The film properties were measured in accordance with the corresponding standard test methods as indicated. These include the thickness (ASTM D1186), gloss (ASTM D523-80), and cross-cut adhesion (DIN 53151).

Preparation of acetophenone formaldehyde resin

Acetophenone formaldehyde resin (AFR) was prepared according to the procedures described earlier.^{4,5} Acetophenone formaldehyde resin (AFR) was prepared in a three-necked flask. Acetophenone (1 mol) and formaldehyde (2 mol) were added and heated to 60°C, while stirring. Then added was 2 mL of 20% NaOH in dropwise manner. When the temperature of the mixture rose to 80–90°C, refluxing began. After 16 h, the reaction was completed for acetophenone formaldehyde resin. The resin was purified by decanting the upper phase and washing several times with hot water. It was then dried at 100°C under vacuum. The number of OH groups per mole of AFR is less than 3, and there are two reactive sites (yield 70%) (M_n GPC: 750).

Bromination of acetophenone formaldehyde resin (AFRBr)

Under nitrogen 2.6 mL, (0.025 mol) 2-bromopropionyl bromide was added dropwise to a stirring mixture of acetophenone formaldehyde resin (10.42 g, 0.01 mol) and triethylamine (1.7 mL, 0.012 mol) in 80 mL of CHCl_3 in an ice bath for 1 h. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 h. The reaction mixture was washed with water (3×80

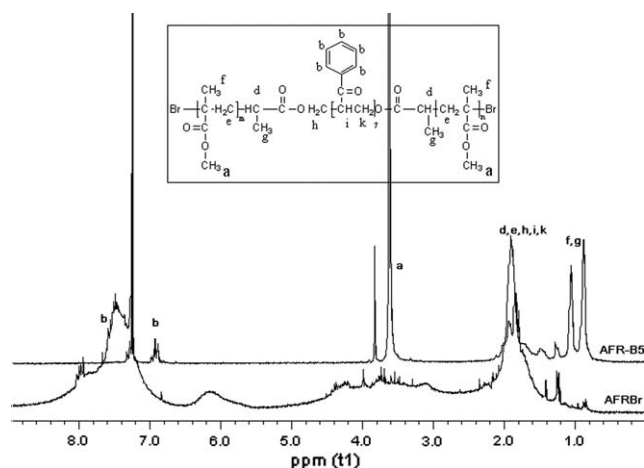


Figure 2 $^1\text{H-NMR}$ spectrum of AFRBr macroinitiator and AFR-B triblock copolymer in CDCl_3 .

TABLE I
Copolymerization of MMA with Acetophenone Formaldehyde Resin

Run ^a	Time (min)	Conv. (%)	[Mo]/[Io]	% MMA ^c (mol)	M_n^b	$M_n^{\text{NMR}^c}$	M_w/M_n^b
AFR-B1	30	14	200	93	13,180	7508	1.27
AFR-B2	60	17	200	95	12,190	14,071	1.36
AFR-B3	120	19	200	94	24,340	12,514	1.38
AFR-B4	30	43	100	88	13,720	8143	1.39
AFR-B5	120	79	100	96	19,800	7797	1.40

^a In anisole, 90°C.

^b Determined from GPC, based on PMMA standards.

^c Calculated by ¹H-NMR.

mL) and then dried over MgSO₄. After filtration and evaporation of CHCl₃, dark red product was obtained. It was dissolved in acetone and precipitated into the hexane. It was dried under vacuum.

Synthesis of ABA type block copolymers by ATRP (AFR-B)

To a schlenk tube equipped with a magnetic stirrer, vacuum, and dry nitrogen was applied three or four times, then certain amounts of MMA, anisole, ligand, PMDETA, and macroinitiator acetophenone formaldehyde resin were added in the order mentioned under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gasses and then tube was immersed in an oil bath and held by a thermostat at 90°C, with rigorous stirring. The polymerization was performed for a determined time. Then the tube was cooled to room temperature and the contents were dissolved in large amount of THF. The THF solution was passed through a short neutral alumina column to remove copper complex and then excess THF was removed by evaporation. The polymer was precipitated into excess methanol, isolated by vacuum filtration and dried at room temperature in vacuum for 24 h. The conversion was determined gravimetrically.

RESULTS AND DISCUSSION

In this study, ABA type block copolymers were first prepared by copolymerization of bromide functionalized AFR with MMA. Atom transfer radical polymerization (ATRP) was used to synthesize block copolymers having acetophenone formaldehyde resin and poly(methylmethacrylate) (PMMA). In the first step, AFR resin was modified with the transformation of the hydroxyl terminal into a reactive C—Br terminal with 2-bromopropionyl bromide (Scheme 1). It is well known that 2-bromopropionates are initiators for ATRP with a high initiating efficiency.^{27,43,44}

The structure of the product (AFRBr) was confirmed by spectroscopic investigations. The FT-IR spectrum of AFRBr indicated no signal corresponding to —OH groups of the starting AFR and gave the characteristic CO ester band at 1720 cm⁻¹ (Fig. 1).

As a second step, AFR having 2-bromopropionyl functionality was used as macroinitiator to initiate ATRP of MMA to prepare ABA type block copolymers as mentioned previously (Scheme 2).

¹H-NMR spectrum recorded in CDCl₃ evidenced resonance signals of —CH₃, —CH₂, —OCH₂, and aromatic group of AFRBr with protons of relative intensities corresponding to the number and type of protons. The copolymer composition was analyzed with ¹H-NMR. The spectrum was illustrated in

TABLE II
Data of the ATRP of MMA, in Anisole Solution at 90°C for Kinetic Plot

Run	Time (min)	Conv. (%)	[Mo]/[Io]	M_n^a	M_w/M_n^a
AFR-B6	30	15	200	14,700	1.32
AFR-B7	60	19	200	16,830	1.30
AFR-B8	120	32	200	25,300	1.26
AFR-B9	30	36	100	13,500	1.30
AFR-B10	60	54	100	15,700	1.28
AFR-B11	120	68	100	20,600	1.26

^a Determined from GPC, based on PMMA standards.

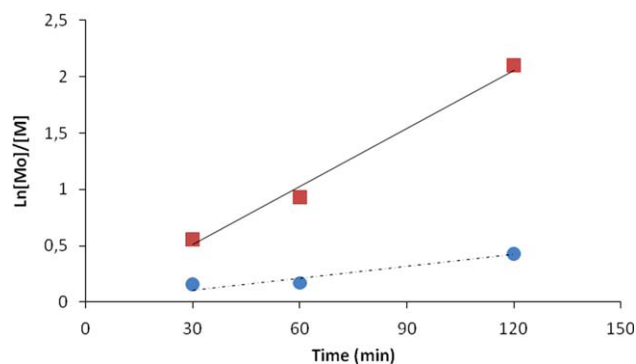


Figure 3 First-order plots for the polymerization of AFRBr resin with MMA using CuBr catalyst in anisole solution at 90°C. ■, [M]/[I]/[Cu]/[PMDETA] = 100/1/1/2; ●, [M]/[I]/[Cu]/[PMDETA] = 200/1/1/2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. The signals observed at 3.58 ppm correspond to the methyl of the ester group of MMA, and the peaks 6.5–8.0 ppm are assigned to aromatic protons of acetophenone ring. Spectrum indicated the presence of $-\text{CH}_3$ protons at 1.7 ppm, $-\text{CH}_2-$, $-\text{CH}$ protons at 2.2–2.3 ppm. Signals due to the $-\text{CH}-\text{Br}$ protons $\delta = 4.1$ ppm of the macroinitiator were also shifted to $\delta = 2.0$ ppm, which indicated the consumption of bromide in ATRP of MMA. (Fig. 2)

Block copolymerization was carried out in anisole with CuBr/PMDETA complexes as the catalyst at 90°C. Typical results concerning the ATRP of MMA are presented in Tables I and II. M_n values of AFR and macroinitiator AFRBr, determined by GPC were 750 and 900, respectively.

During the copolymerization of AFRBr with MMA for 30, 60, and 120 min with the 200 or 100 macroinitiator ratios, the average molecular weights increased to 12190 and 24340, whereas polydispersity values did not change sharply to 1.27–1.40. These results were also good agreement with MMA percentage of the block copolymers.

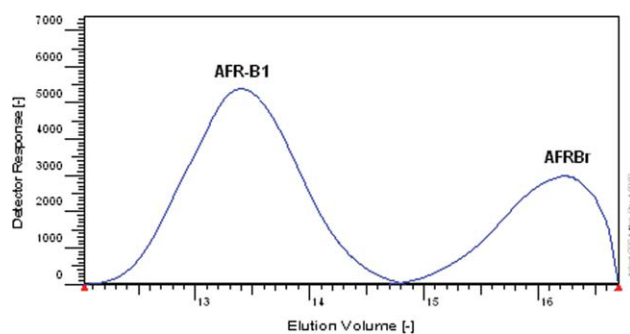


Figure 4 GPC traces of AFRBr macroinitiator and corresponding triblock (PMMA-*b*-AFR-*b*-PMMA) copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
DSC and TGA Results for AFR Resin and Related Copolymers

Samples	T_g (°C) ^a	T_m ^a	$T_{\%50}$ (°C) ^b	Residue (%) at 500°C ^b
AFR	47	68	346.5	18.3
AFRBr	72	99	396.2	36.9
AFR-B1	114	–	402.5	6.0
AFR-B2	113	–	400.1	6.3
AFR-B3	113	–	390.8	6.0
AFR-B4	84	–	396.2	6.7
AFR-B5	104	–	388.1	5.2

T_g , glass transition temperature; T_m , melting point.

^a Detected by DSC.

^b Detected by TGA.

Also kinetic plot was generated for AFR-B copolymers (AFR-B6, AFR-B7, AFR-B8, AFR-B9, AFR-B10, and AFR-B11) due to the same polymerization conditions (Table II and Fig. 3). Monomer conversion is measured by gravimetry by drying the sampled AFR-B copolymer solution to constant weight in a vacuum oven at room temperature.

Figure 3 shows the first-order kinetic plots for the polymerization of AFRBr resin with MMA using CuBr catalyst in anisole solution at 90°C. The linearity of the plots suggests that the polymerizations of MMA monomer proceed in a controlled and living manner.

In GPC analyses, the increase in M_n value of AFRBr showed the copolymer formation (Fig. 4). Polydispersities of the corresponding copolymers (AFR-B1, AFR-B2, AFR-B3, AFR-B4, and AFR-B5) remained roughly the same with the precursor polymers. (Table I)

Thermal behaviors of polymers were checked with DSC and TGA measurements. The results of thermal analysis are summarized in Table III. In DSC thermograms of AFR and AFRBr, we observed two

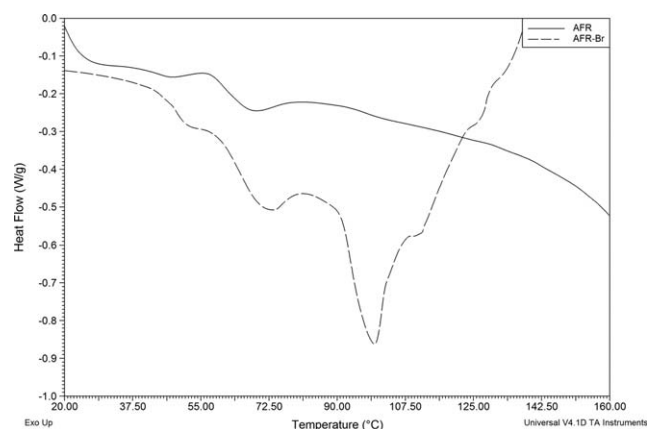


Figure 5 DSC thermograms of AFR resin and AFRBr macroinitiator.

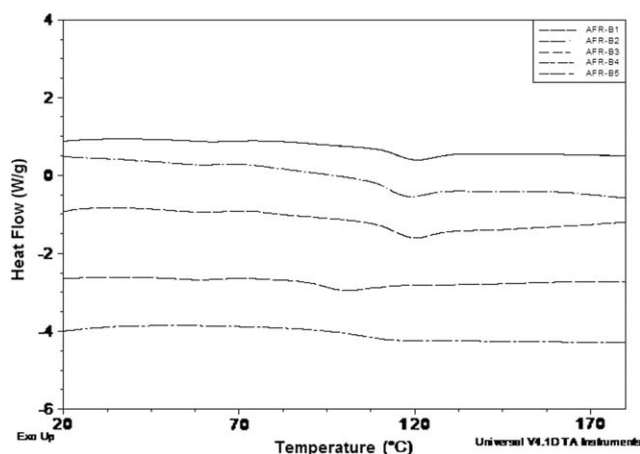


Figure 6 DSC thermograms of triblock (PMMA-*b*-AFR-*b*-PMMA) copolymers.

endothermic events; one occurring at 47°C and 68°C corresponded to the T_g and T_m of AFR. (Fig. 5)

The introduction of bromide units into the AFR polymers was expected to improve their thermal stability because of the incorporation of the bromide into the backbone. T_g and T_m values of the AFRBr increased up to 72°C and 99°C, respectively, due to the bromide group effect, higher weight loss (T_{50}) temperature and higher residue indicated that AFRBr exhibited better thermal stability than that of AFR. (Table III).

Thermal behavior of block copolymers was examined by differential scanning calorimeter in the range of 20–200°C (Fig. 6). DSC measurement on block copolymers exhibited only one glass transition, indicating that the resulting copolymers are ABA type copolymers.

Molecular weights of AFR-B1 and AFR-B4 are closed to each other. However, AFR-B1 and AFR-B4 have different MMA content in copolymer composition. Introduction of around 93% MMA in copoly-

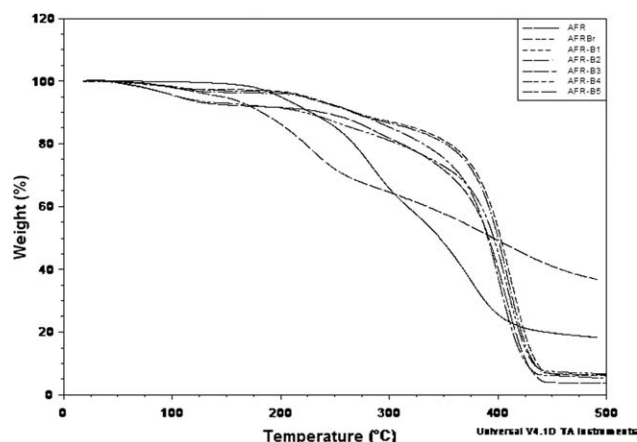


Figure 7 TGA thermograms of AFR, AFRBr, and corresponding triblock (PMMA-*b*-AFR-*b*-PMMA) copolymers.

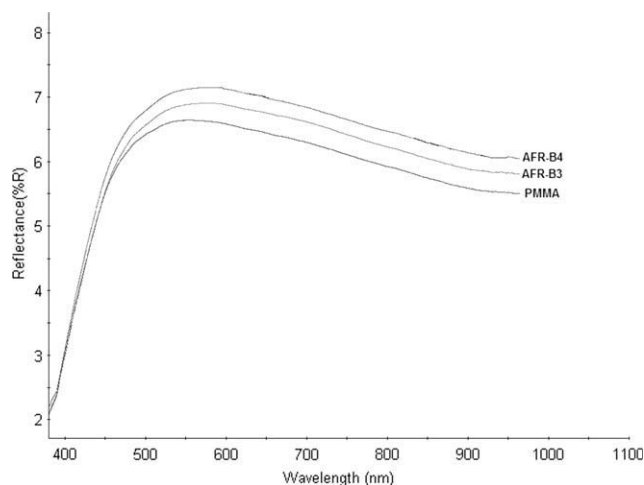


Figure 8 Reflectance's of PMMA, AFR-B3, and AFR-B4 copolymers.

mer increases the T_g value to 114°C, whereas 88% MMA content decreases the T_g value to 84°C (Table III).

The TGA measurements provided a better explanation for the contribution of bromine terminated AFR polymer and ABA type block copolymer formation (Fig. 7). The 50% weight loss temperature was assumed as a measurement of thermal stability and the related results are presented in Table III. All selected block copolymers indicated a higher T_{50} relative to their precursor polymers (AFR, AFRBr) and left residue in a lower ratio than their precursor polymers due to the much pronounced effect of the MMA units.

Polymers were coated on plexiglass®/glass substrates by using spincoater instrument to evaluate the coating properties such as reflectance value, cross-cut adhesion test, and gloss value of block copolymers.

Reflectance values of AFR-B4 higher than that of the AFR-B3 and standard PMMA reflectance values depending on the AFR resin content in block copolymer (Fig. 8). Increasing of reflectance values is related to resin contents in copolymers. Reflectance of films increase because of the percentage of resin is higher than the block copolymer, which has lower molecular weight.

TABLE IV
Physical Characterizations of Resin-Copolymer Films

Sample	Thickness (μm)	Gloss 60°	Cross-cut adhesion
PMMA	13	140	0
AFR-B1	13	114	1
AFR-B2	13	102	0
AFR-B3	15	99	0
AFR-B4	16	90	1
AFR-B5	14	100	0

To obtain a qualitative impression of the adhesion between the block copolymer and the plexiglass® substrate, the cross-cut test was applied according to the DIN 53151 standard. Adhesion can be classified from 0, which represents a good adhesion, to 5, which represents a poor adhesion. All block copolymers exhibited good adhesion on plexiglass® panels. Table IV shows that the adhesions of all resin copolymers on plexiglass were classified to be between 0 and 1.

Coatings gloss is a complex phenomenon resulting from the interaction between light and the surface of the coating. The gloss is affected strongly by surface roughness. Depending on the AFR content of the block copolymer, gloss value and cross-cut adhesion did not change sharply.

In conclusions, synthesis of acetophenone formaldehyde resin containing block copolymers by using condensation and ATRP sequential routes was achieved. Resulting ABA type block copolymers may provide an opportunity for a new breakthrough in the area of polymeric materials for advanced technologies. Our work can be regarded as block copolymers by condensation-ATRP combination in living/controlled radical polymerization. These block copolymers may exhibit different properties due to incorporation of ketonic resins into the block copolymer structure.

References

1. Kravets, V. P.; Chervenyuk, G. I. *Lakokrasochnye Materialy i ikh Primenenie* 1963, 6, 4.
2. Bar, V.; Seregi, G.; Esztergali, E. *Hung. Pat. HU 48284* (1989), *Invs.*; *Chem Abstr* 1990, 112, 21732m.
3. Stoye, D.; Freitag, W., Eds. *Resins for Coatings: Chemistry, Properties and Applications*; Munich: Hanser Publications, 1996; p 167.
4. Kizilcan, N.; Galioglu, O.; Akar, A. *J Appl Polym Sci* 1993, 50, 577.
5. Kizilcan, N.; Akar, A. *J Appl Polym Sci* 1996, 60, 465.
6. Kizilcan, N.; Akar, A. *J Appl Polym Sci* 2005, 98, 97.
7. Ustamehmetoglu, B.; Kizilcan, N.; Saraç, S.; Akar, A. *J Appl Polym Sci* 2001, 82, 1098.
8. Kizilcan, N.; Ustamehmetoglu, B. *J Appl Polym Sci* 2005, 96, 618.
9. Uyanik, N.; Kizilcan, N.; Akar, A. *J Appl Polym Sci* 1998, 67, 643.
10. Uyanik, N.; Yildirim, H.; Kizilcan, N.; Akar, A. *Angew Macromol Chem* 1991, 191, 1.
11. Uyanik, N.; Yalçinkaya, H.; Kizilcan, N. *Surf Coat Interface Part B: Coat Trans* 2001, 84, B4.
12. Kizilcan, N.; Akar, A. *J Appl Polym Sci* 2002, 85, 500.
13. Kizilcan, N.; Akar, A. *J Appl Polym Sci* 1999, 72, 927.
14. Ergun, S.; Kizilcan, N.; Onen, A. *J Appl Polym Sci* 2007, 105, 1012.
15. Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, M. G. *Macromolecules* 1987, 20, 1473.
16. Wang, G.; Huang, J. *Macromol Rapid Commun* 2007, 28, 298.
17. Szwarc, M. *Adv Polym Sci* 1960, 2, 275.
18. Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1984, 17, 265.
19. Georges, M. K.; Veregin, R.; Dazmaier, P.; Hamer, G. *Macromolecules* 1993, 26, 2987.
20. Gaynor, S.; Matyjaszewski, K.; Wang, J. S. *Macromolecules* 1995, 28, 8051.
21. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
22. Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* 1996, 272, 866.
23. Patten, T. E.; Matyjaszewski, K. *Acc Chem Res* 1999, 32, 895.
24. Matyjaszewski, K. *Chem Eur J* 1999, 5, 3095.
25. Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog Polym Sci* 2001, 26, 337.
26. Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
27. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
28. Zhao, L.; Zhang, J.; Jiang, J.; Chen, C.; Xi, F. *J Polym Sci* 2002, 40, 3360.
29. Jankova, K.; Chen, X.; Kops, J.; Batsberg, W. *Macromolecules* 1998, 31, 538.
30. Jankova, K.; Bednarek, M.; Hvilsted, S. *J Polym Sci* 2005, 43, 3748.
31. Ibrahim, K.; Löfgren, B.; Seppala, J. *Eur Polym J* 2003, 39, 2005.
32. Ibrahim, K.; Löfgren, B.; Seppala, J. *Eur Polym J* 2003, 39, 939.
33. Zhao, L.; Chen, C.; Xi, F. *J Polym Sci* 2003, 41, 2156.
34. Fukuda, T.; Goto, A.; Tsujii, Y.; Miyamoto, T. *Macromolecules* 1996, 29, 3050.
35. Yoshida, E. *J Polym Sci Part A: Polym Chem* 1996, 34, 2937.
36. Serhatli, I. E.; Kacar, T. *J Appl Polym Sci* 2006, 99, 3187.
37. Hawker, J. J. *Angew Chem Int Ed Engl* 1995, 34, 1456.
38. Cakir, T.; Serhatli, I. E.; Onen, A. *J Appl Polym Sci* 2006, 99, 1993.
39. Cakir, T.; Onen, A.; Serhatli, I. E. *J Appl Polym Sci* 2008, 107, 2074.
40. Kita, Y. *J Appl Polym Sci* 1997, 63, 363.
41. Doi, T.; Sugiura, Y. *J Appl Polym Sci* 1996, 61, 853.
42. Genyuan, Z. *New Chem Mater* 1995, 5, 3.
43. Xu, Y. A.; Xue, H.; Ding, J. Y.; Gao, L. X.; Ding, M. X. *Chin Chem Lett* 2003, 14, 141.
44. Verma, H.; Kannan, T. *Polym J* 2008, 40, 867.
45. Li, P.; Li, Z.; Huang, J. *Polymer* 2007, 48, 1557.
46. Luo, Z.-H.; Yu, H.-J.; He, T.-Y. *J Appl Polym Sci* 2008, 108, 1201.
47. Luo, Z.-H.; He, T.-Y. *React Funct Polym* 2008, 68, 931.