Synthesis of Cyclohexanone Formaldehyde Resin-Methylmethacrylate Block-Graft Copolymers via ATRP

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ABSTRACT: Well defined block-graft copolymers of cyclohexanone-formaldehyde resin (CFR) and methylmethacrylate (MMA) were prepared via atom transfer radical polymerization (ATRP). In the first step, cyclohexanone formaldehyde resin (CFR) containing hydroxyl groups were modified with 2-bromopropionyl bromide. Resulting multifunctional macroinitiator was used in the ATRP of MMA using copper bromide (CuBr) and N,N,N',N'',N''-pentamethyl-diethylenetriamine (PMDETA) as catalyst system at 90°C. The chemical composition and structure of the copolymers were characterized by nuclear magnetic resonance (^{1}H-NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and molecular weight measurement. Molecular weight distributions of the CFR graft copolymers were measured by gel permeation chromatography (GPC). M_n values up to 19,000 associated with narrow molecular weight distributions (polydispersity index (PDI) $<$ 1.6) were obtained with conversions up to 49%. Coating properties of synthesized graft copolymers such as adhesion and gloss values were measured. They exhibited good adhesion properties on Plexiglas substrate. The thermal behaviors of all polymers were conducted using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2628–2635, 2012

**Key words:** cyclohexanone formaldehyde resin; ATRP; block copolymers

INTRODUCTION

Numerous reports about aliphatic and alicyclic ketone-formaldehyde resins exist for many commodity applications like paints, foam, adhesives, and molding materials.[1–6] Cyclohexanone-formaldehyde resin (CFR) has good utility because it has excellent glossy and transparent properties.[3,4] Due to their high compatibility and solubility with wide range of film formers, resins (CFR) play a key role in the field of coatings (paints, inks, varnish, lacquers,[7–11] and light stabilizers,[12]) as a blend for the improvement of coating properties,[13–15] and as an adhesive in multilayered laminated sheets. Synthesis of ketonic resin containing copolymers has been extensively studied[16–24] since the ketonic resin segments improves adhesive, solubility, gloss, and light stability of parent polymers. In a recent communication, we briefly reported the synthesis of well-defined acetophenone-formaldehyde resin containing ABA type block copolymers by atom transfer radical polymerization (ATRP).[25]

Polymethylmethacrylate (PMMA) is often used as a light or shatter-resistant alternative to glass. It is often preferred because of its moderate properties, easy handling and processing, and low cost. PMMA is a versatile material and has been used in a wide range of fields and applications as a substituent of glass, medical technologies and implants and esthetic use as well.[26–29] This properties and uses of PMMA motivated us to work on.

In recent years, living free-radical polymerization,[30–35] especially copper-based ATRP,[36–41] has received a great deal of attention in the literature because of its monomer versatility, simplicity in practice, controllability with respect to molecular parameters, and so forth. The ATRP process uses an alkyl halide as initiator, and a metal in its lower oxidation state with complexing ligands. The process involves the successive transfer of the halide from the dormant polymer chain to the ligated metal complex, thus establishing a dynamic equilibrium between active and dormant species which lead to yield polymers with low polydispersity and controlled molecular weight. It has successfully been used to prepare a wide range of products with various chain architectures, such as linear, star, block-star, dendritic, highly branched, and comb architectures,[42] and various compositions. Block-graft copolymers, including comb-like copolymers,

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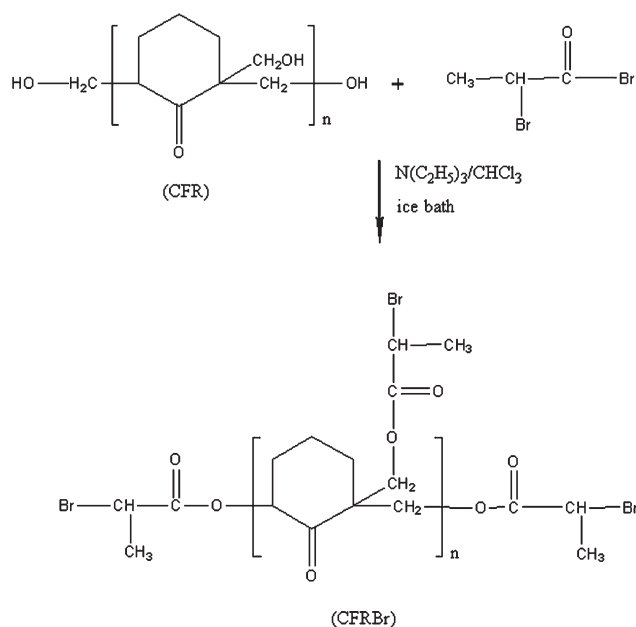
Scheme 1 Synthesis of CFRBr.

are a type of special block copolymer with a lot of side chains covalently grafted to a backbone or main chain.[43–47] Currently, there are three approaches for the synthesis of graft copolymers: "grafting through" (the polymerization of macromonomers), "grafting onto" (the addition of previously prepared side chains to a backbone), and "grafting from" (the polymerization of side chains from a macroinitiator backbone).[48] "Grafting from" synthesis of graft polymers starts with the preparation of a backbone polymer (macroinitiator) with a predetermined number of initiation sites that is subsequently used to initiate polymerization of the side chains. The macroinitiator can be prepared directly or by first preparing a precursor that is subsequently functionalized to include initiating moieties which we did for the cyclohexanone formaldehyde resin.

In this article, functional block-graft copolymers containing ketonic resin were prepared through the atom transfer polymerization of CFR with methyl methacrylate (MMA). For this purpose, bromine functional resin was synthesized by esterification of CFR with 2-bromopropionyl bromide. After functionalization of the CFR, it is used as a macroinitiator for block-graft copolymerization of MMA.

EXPERIMENTAL

Tetrahydrofuran (J. T. Baker, Netherland) was dried over potassium hydroxide and distilled over CaH_2. Chloroform (J. T. Baker, Netherland) 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, Canada) 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, Canada), acryloyl chloride (99% Aldrich, Canada), copper(I)-bromide (98%, Aldrich), anisole (99% Acros), triethylamine (99% Acros, Belgium), 2-bromopropionyl bromide (97% Aldrich, Canada), acetophenone (99% Merck), and formaldehyde 37% solution (Fluka, Canada), were used without further purification.

Analysis

Fourier transform infrared (FTIR) spectra were measured using model recorded Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer. ^{1}H-NMR spectra were measured on a Bruker AC (250 MHz, Darmstadt, Germany) spectrometer by using 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 comparing the integration ratio of —CH_2 protons of cyclohexanone resin to methoxy protons of pMMA. 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 mm × 250 mm, 5 micron) measuring in the range of 10^4–10^6, 3×10^3–3×10^5, 5×10^2–10^4, respectively. THF was used as the eluent at a flow rate of 0.5 mL/min at 30°C. The molecular weights (MWs) of the polymers were calculated with the aid of polystyrene standards. The thermal properties of the copolymers were measured by differential scanning calorimeters (TA, DSC Q10) in a flowing nitrogen atmosphere from 20 to 180°C at scanning rate of 10°C/min. Thermal stability of copolymers was measured by thermo gravimetric analysis (TA, TGA Q50) in a flowing nitrogen atmosphere from 30
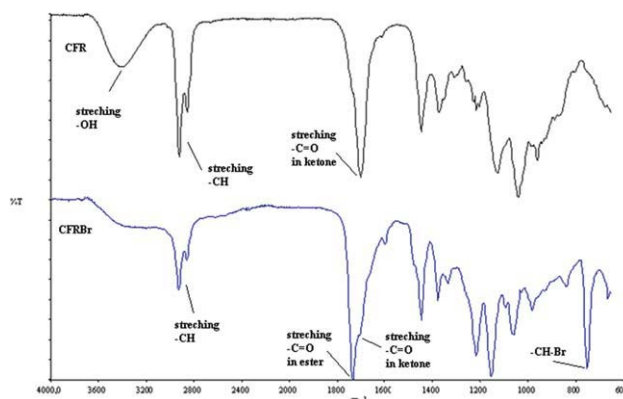
Figure 1 FTIR spectrum of CFR resin and CFRBr macroinitiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
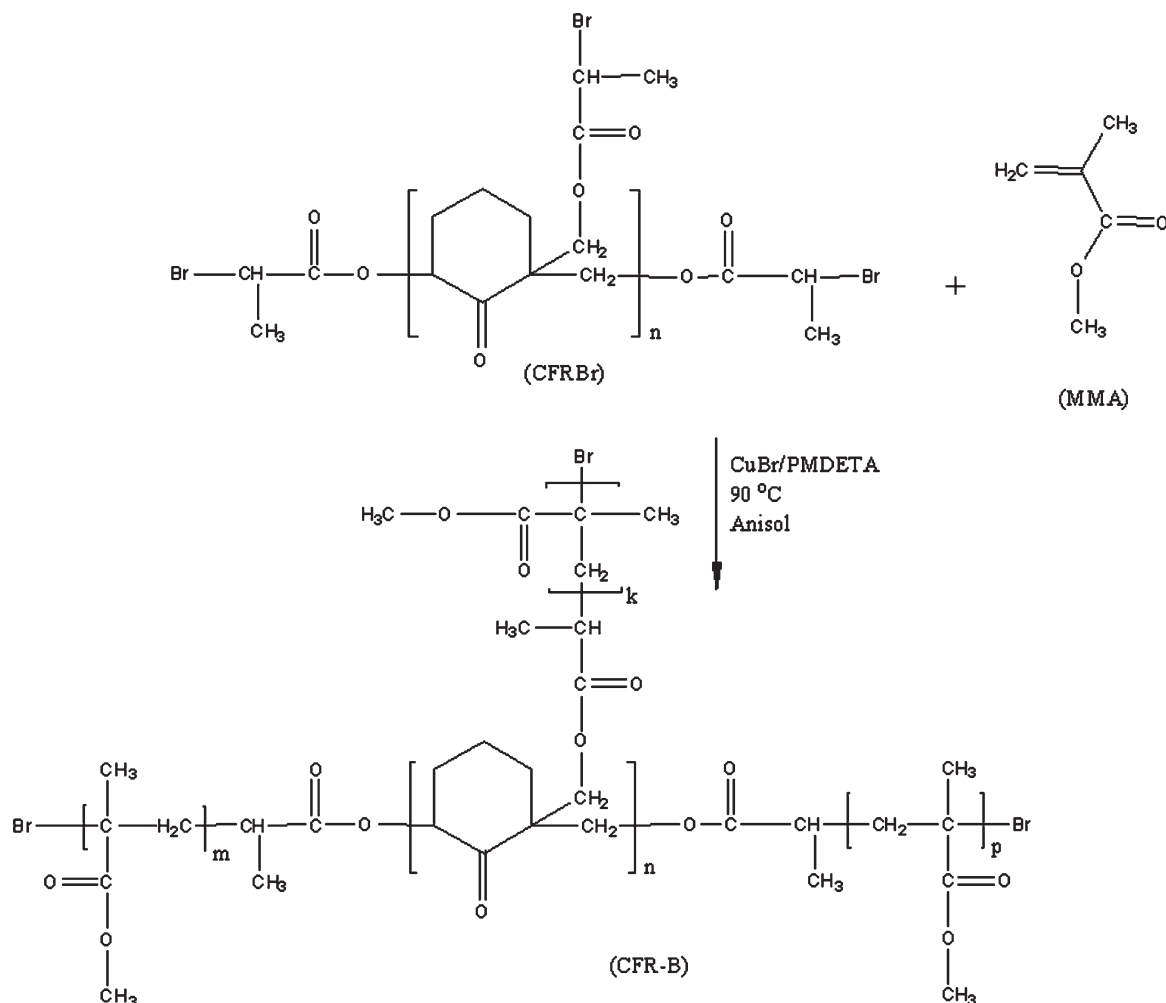
Scheme 2 Synthesis of CFR-B.

to 500°C at heating rate of 20°C/min. Copolymer resin films were prepared by using SCS Spincoater P6700 instrument. The film properties were measured in accordance with the corresponding standard test methods as indicated. These include the thickness (ASTM D-1186), gloss (ASTM D-523-80), and crosscut adhesion (DIN 53151).

Preparation of cyclohexanone-formaldehyde resin

CFR was prepared according to the procedures described earlier.[49] CFR was prepared in a three-necked flask. Ketone (1 mol) and formaldehyde (1.6 mol) were added and heated to 60°C, while stirring. Then 2 mL of 20% NaOH was added in equal portions. When the temperature of the mixture rose to 80–90°C, refluxing began. After 3 h, the reaction was completed. After complete reaction time, two layers were formed. The modified resin was separated and purified by decanting the water layer and washing several times with warm water, and dried by vacuum at about 100°C (yield 65%, M_n^{GPC} = 1000 g/mol, PDI = 1.1).

Bromination of cyclohexanone-formaldehyde resin (CFRBr)

Under nitrogen 9.3 mL (0.088 mol) 2-bromopropionyl bromide was added dropwise to a stirring mixture of CFR (10.96 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 mL) and then dried over MgSO$_4$. After filtration and evaporation of CHCl$_3$ dark red product was obtained. It was dissolved in acetone and precipitated into the hexane. It was dried under vacuum (yield 43%, M_n^{GPC} = 1400 g/mol, PDI = 1.53).

Synthesis of CFR block-graft copolymers by ATRP (CFR-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, cyclohexanone
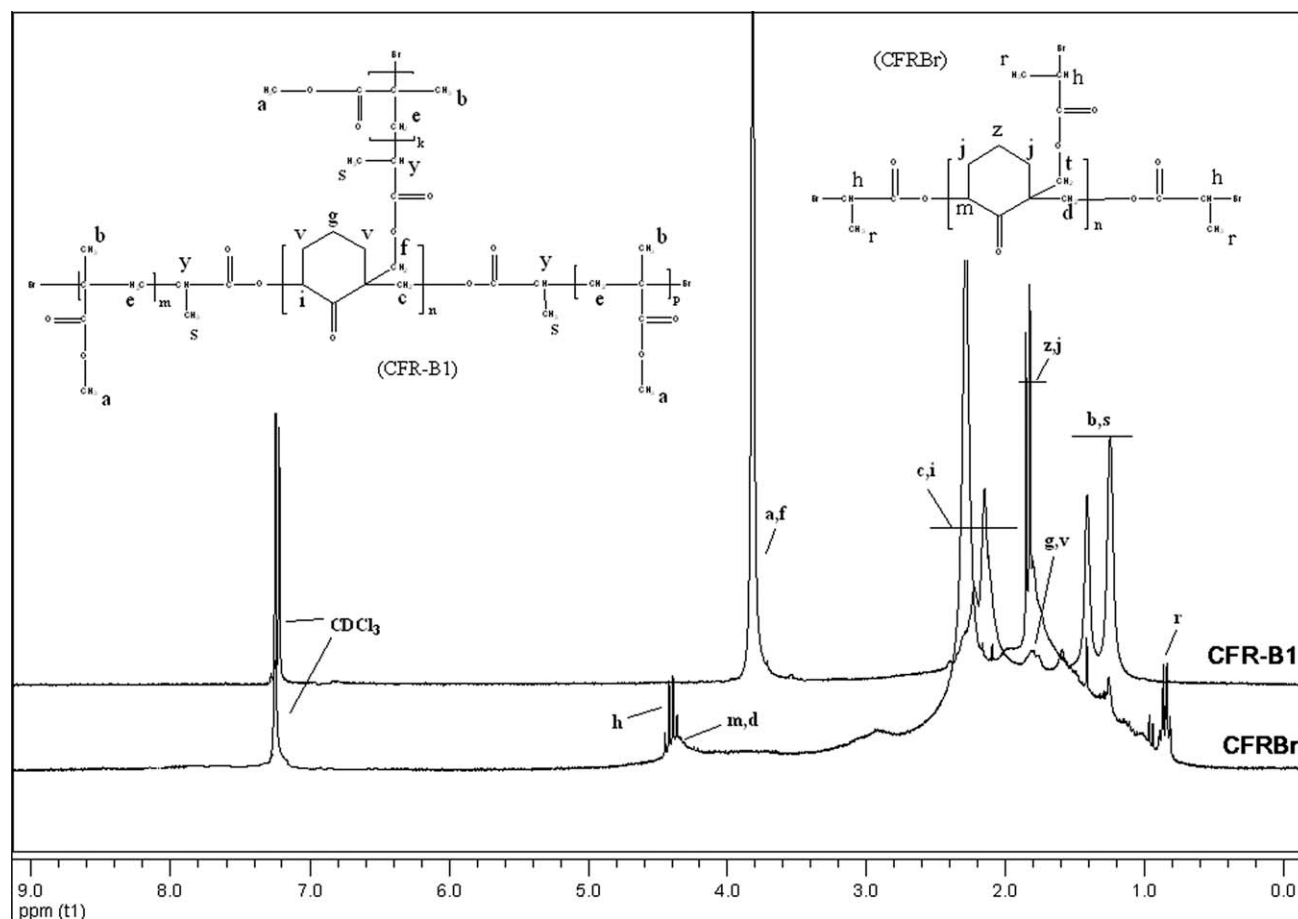
Figure 2 ^{1}H-NMR spectrum of CFRBr macroinitiator and CFR-B1 graft copolymer in CDCl$_3$.

formaldehyde resin, were added in the order mentioned under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases 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, block-graft copolymers were firstly synthesized by copolymerization of bromide functionalized cyclohexanone-formaldehyde resin (CFR) with methylmethacrylate (MMA) via atom transfer

TABLE I
Copolymerization of MMA with Cyclohexanone Formaldehyde Resin

Run[a]	Time (min)	Conv[b] (%)	[Mo]/[Io]	MMA %[c] (mol)	M_n[d] (g/mol)	M_w/M_n[d]	M_n^{NMRc}
CFR-B1	30	21	100	67	18,900	1.61	15,600
CFR-B2	120	25	100	69	19,200	1.62	15,900
CFR-B3	240	29	100	70	18,400	1.68	16,000
CFR-B4	30	36	200	68	13,800	1.34	12,900
CFR-B5	60	43	200	58	15,300	1.47	18,100
CFR-B6	120	49	200	60	16,500	1.48	18,900

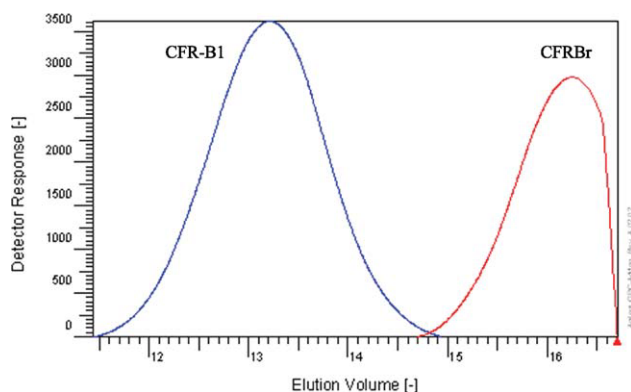[a] In Anisole, 90°C.
[b] Calculated by gravimetry by drying to constant weight in a vacuum oven at room temperature.
[c] Calculated by ^{1}H-NMR.
[d] Determined from GPC, based on PSt standards.

Figure 3 GPC traces of CFRBr macroinitiator and corresponding MMA-CFR block-graft copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

radical polymerization (ATRP). In the first step, CFR having hydroxyl functionality was modified with the transformation of the hydroxyl terminal into a reactive C—Br terminal with 2-bromopropionyl bromide (Scheme 1).

The formation of bromine functional groups was also supported by Fourier transform infrared (FTIR) analysis. The spectra of CFRBr showed the carbonyl stretch of ester structure at 1720 cm^{-1} and C—Br stretch at 725 cm^{-1} after bromination (Fig. 1). The peak at 3450 cm^{-1} which belongs to hydroxyl group of cyclohexanone resin had nearly disappeared.

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

^{1}H-NMR spectra of CFRBr and CFR-B recorded in CDCl$_3$ are shown in Figure 2. From the NMR spectrum of —CFRBr, we can say that it is fully brominated, because hydroxyl group signal of —CH$_2$—OH is not seen in the spectrum which would be at 3.2–4.2 ppm. The signal at 4.36–4.44 ppm corresponds to CH—Br protons in the structure. Consumption of these bromine groups by initiation in ATRP was confirmed in the graft copolymers of MMA. Number of repeating units and molecular weight (M_n^{NMR}) of CFRBr were calculated as 4 and 1404, respectively, by the integration ratio of CH—Br protons (h) to —CH$_2$ protons (z,j) of cyclohexanone ring from the ^{1}H-NMR spectrum.

The ^{1}H-NMR spectrum of CFR-B1 indicated the presence of both monomers in the final copolymers and allowed for quantitative determination of the amount of incorporated second monomer (MMA). For the obtained block-graft copolymers (CFR-B), the spectrum displayed the expected resonances for methoxy group of MMA at 3.58 ppm, —CH$_3$ protons at 0.8–1.2 ppm and aliphatic —CH$_2$ protons of cyclohexanone ring at 1.80–1.87 ppm. The M_n of the

block-graft copolymers can be calculated by comparing the integration of signals of characteristic —OCH$_3$ protons (a) in MMA with —OCH$_2$ (g,v) protons in CFR resin (Table I).

Block-graft copolymerization of cyclohexanone resin and MMA were performed with CuBr/PMDETA complexes as catalyst in anisole at 90°C. Films of these copolymers were prepared. These films were transparent, indicating that there was no macroscopic phase separation and no formation of large amounts of homopolymer.

Gel permeation chromatography (GPC) curve of the copolymerization product shifted to the high molecular weight side compared to that of the CFBr precursor. The monomodal shape of the GPC trace of the obtained copolymer suggests the formation of graft copolymer without homopolymerization (Fig. 3).
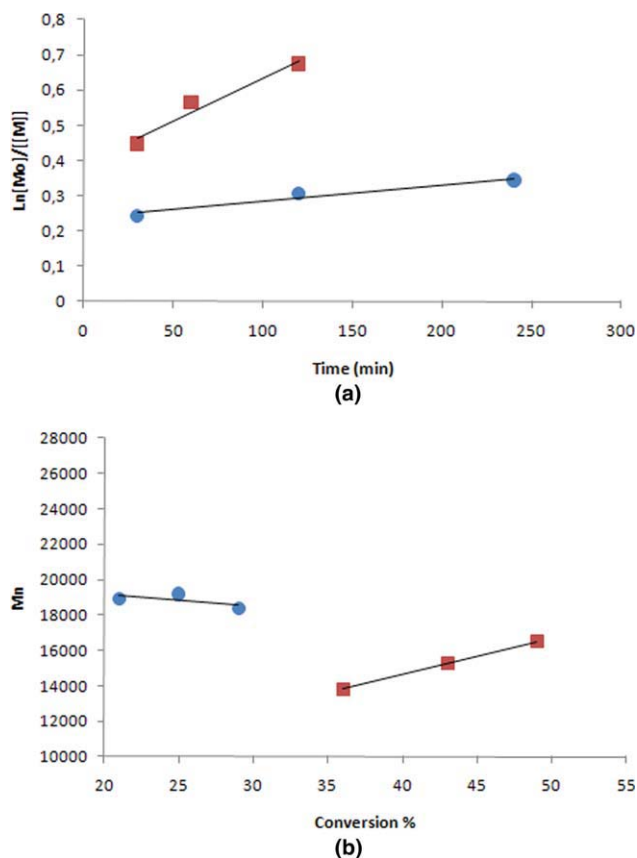
Figure 4 (a) First-order plots for the polymerization of CFRBr resin with MMA using CuBr catalyst in anisole solution at 90°C. [MMA] = 3.71M, ■ [MMA]/[I]/[Cu]/[PMDETA] = 200/1/1/2, ● [M]/[I]/ [Cu]/[PMDETA] = 100/1/1/2. (b) Number average molecular weight as a function of conversion for the polymerization of CFRBr resin with MMA using CuBr catalyst in anisole solution at 90°C. [MMA] = 3.71M, ■ [MMA]/[I]/[Cu]/[PMDETA] = 200/1/1/2, ● [M]/[I]/ [Cu]/[PMDETA] = 100/1/1/2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
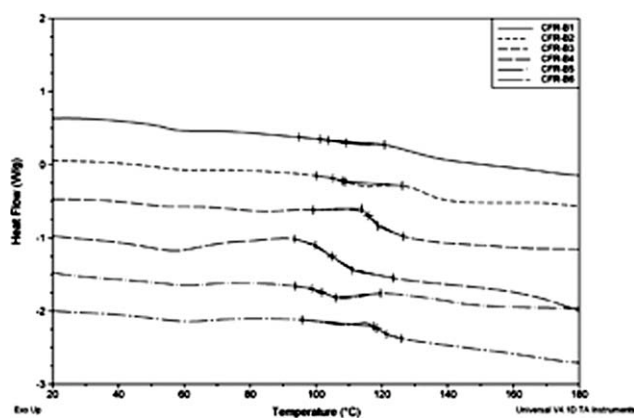
Figure 5 DSC thermograms of MMA-CFR block-graft copolymers.

Typical results concerning the ATRP of MMA are presented in Table I. M_n values of CFR and macroinitiator, CFRBr, determined by GPC were 1000 g/mol and 1400 g/mol, respectively. Monomer conversion is measured by gravimetry by drying the sampled CFR-B copolymer solution to constant weight in a vacuum oven at room temperature.

During the copolymerization of CFRBr with MMA for 30, 60, 120, and 240 min with the 200 or 100 macroinitiaors ratios, the average molecular weights increased to 13,800, 19,200 whereas polydispersity values did not change sharply to 1.34–1.68. Because of the high density of the branches in the polymers, GPC data analysis with RI detection calibrated versus linear PSt standards does not yield accurate molecular weight data. Such graft copolymers always present different hydrodynamic volumes than the corresponding linear polymers. As such, the "grafting from" approach enables preparation of long-backbone molecular brushes with a high grafting density. However, compared to the "grafting through" approach,

"grafting from" allows less control of side chain length and grafting density. "Grafting from" approach involves the polymerization of side chains from a macroinitiator which was also the case of this study.

Also kinetic plots were generated for CFR-B copolymers. Figure 4(a,b) shows the first-order kinetic plots for the polymerization of CFRBr resin with MMA using CuBr catalyst in anisole solution at 90°C. The linearity of the plots suggests that the

TABLE II
DSC and TGA Results for CFR Resin and Related Copolymers

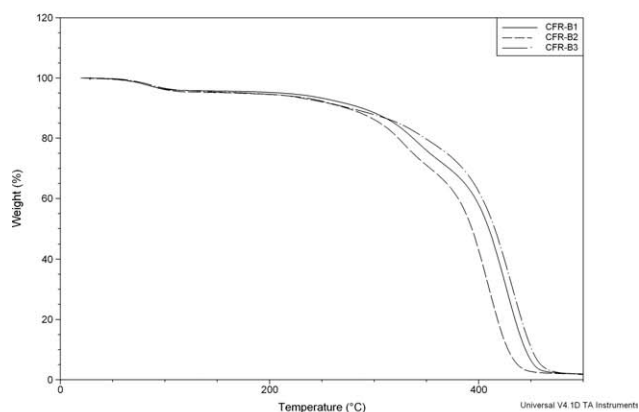| Samples	T_g (°C)[a]	$T_{\%50}$ (°C)[b]	$T_{\%90}$ (°C)[b]	Residue (%) at 500°C[b]
CFR	30	350	428	2.6
CFRBr	nd	387	468	6.0
CFR-B1	109	409	445	1.8
CFR-B2	108	393	428	1.9
CFR-B3	110	385	415	1.7
CFR-B4	105	404	434	2.3
CFR-B5	102	397	430	2.0
CFR-B6	103	377	406	2.1

T_g, Glass transition temperature; nd, not detected.
[a] Detected by DSC.
[b] Detected by TGA.
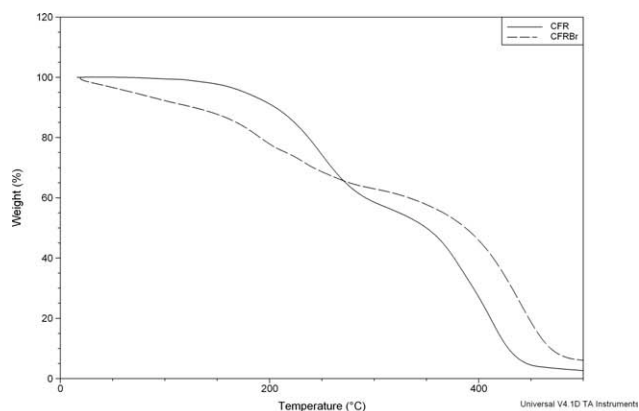
(a)

(b)
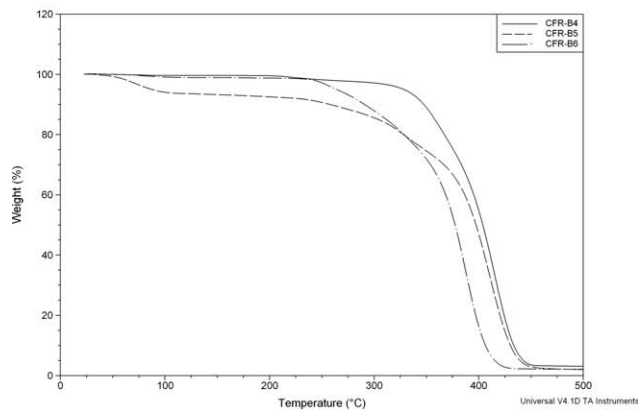
(c)

Figure 6 (a) TGA thermograms of CFR and CFRBr. (b) TGA thermograms of CFRB1-B3 block-graft copolymers. (c) TGA thermograms of CFRB4- B6 block-graft copolymers.

TABLE III
Physical Characterizations of Resin-MMA
Copolymer Films

Sample	Thickness (μm)	Gloss 60°	Cross-cut adhesion
PMMA	13	140	0
CFR	13	80	0
CFR-B1	12	100	0
CFR-B2	16	99	0
CFR-B3	13	110	0
CFR-B4	12	111	0
CFR-B5	12	82	0
CFR-B6	16	86	0

polymerizations of MMA monomer proceed in a controlled and living manner.

Thermal behavior of copolymers was examined by differential scanning calorimetry (DSC) in the range of 20–180°C and by thermogravimetric analysis (TGA) in the range of 30–500°C (Fig. 5) and the related results are presented in Table II.

In DSC thermogram of CFR, we observed only one endothermic peak at 30°C corresponding to the T_g value of the resin, we did not detect any T_g value in the thermogram of CFRBr. Normally, the T_g of the PMMA homopolymer is about 105–120°C. Increasing % MMA content in copolymer increases the T_g value, whereas decreasing % MMA content decreases the T_g value of the block-graft copolymer (Table II). Copolymer CFR-B1 and CFR-B4 showed also a transition nearly at 50–55°C which might belong to the resin part of the copolymer; however, these transitions were not observed during the second heating.

The 50% weight loss temperature ($T_{50\%}$) was assumed as a measurement of thermal stability and all the selected graft copolymers indicated a higher $T_{50\%}$ temperature value relative to their precursor polymers (CFR, CFRBr) and left residue in a lower ratio than their precursor polymers (Fig. 6). Due to the bromide group effect, higher weight loss ($T_{90\%}$) temperature and higher residue indicated that CFRBr exhibited better thermal stability than that of block-graft copolymers.

To evaluate the coating properties such as crosscut adhesion test, gloss value of graft copolymers, the polymer surfaces were coated on Plexiglas®/glass substrates by using spincoater instrument. To obtain a qualitative impression of the adhesion between graft copolymer and the Plexiglas substrate, the crosscut 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 the copolymers exhibited good adhesion on Plexiglas panels. Table III shows that the adhesion of all the resin copolymers on Plexiglas was classi-

fied to be 0. Cyclohexanone formaldehyde resin copolymers showed better adhesion properties than acetophenone formaldehyde resin copolymers which was evaluated in our previous work.[25]

Coatings gloss is a complex phenomenon resulting from the interaction between light and the surface of the coating. The gloss value is affected strongly by surface roughness and also by the resin content. Ketonic resin is known for its light color, good gloss, and excellent light stability. Gloss value of the CFR was measured as 80° in Table III. We found gloss value of PMMA is higher than CFR. Table III shows an increase in gloss of the block-graft copolymer with increasing content of MMA.

CONCLUSIONS

In this study, a new strategy for the synthesis of block-graft copolymer via a combination of condensation and ATRP sequential routes was presented. This synthetic route is a versatile and simple strategy for preparation of block-graft copolymer with well-defined architecture. The obtained polymers have unimodal molecular weight distributions and moderate polydispersity indexes. Work is in progress to extend this preliminary investigation to a more thorough approach, including the industrial applications.

References

1. Tiedemann, G. T.; Sanelemente, M. R. J Appl Polym Sci 1973, 17, 1813.
2. Bordkina, N. I.; Frolov, S. S.; Molkova, G. N.; Izv, V. U. Zavedenii Khim i Khim Teknol 1963, 6, 299.
3. Sato, A. Jpn Kokai 2001, 214, 117.
4. Fhilbin, M.; Albrecht, T.; Norman, G. U.S. Pat. 6,255,369 (2001).
5. Hockhel, R. H. U.S. Pat. 4,183,372 (1974).
6. Harvey, M. T. U.S. Pat. 2,699,431 (1951).
7. Bognar, J.; Kovacs, L.; Szabo, L. Hung. Pat. 55,420 (1991).
8. Bognar, J.; Kovacs, L.; Szabo, L. Hung. Pat. 55,421 (1991).
9. Kurt, F.; Haroo, P.; Hellmuth, K.; Eckehardt, W. U.S. Pat. 4,644,028 (1987).
10. Domenech-Carbo, M. T.; Yusa-Marco, D. J.; Bitossi, G.; Silva, M. F.; Mas-Barbera X. O.; Osete-Cortina, L. Anal Bioanal Chem 2008, 391, 1351.
11. Werner, A.; Andreas, W.; Patrick, G. U.S. Pat. 71,83,372 (2004).
12. Eiichi, H.; Nobuo, T. U.S. Pat. 38,16,140 (1974).
13. Athawale, V. D.; Shetty, N. J. Surf Coat Inter 2000, 4, 168.
14. Athawale, V. D.; Chamankar, A. V. JAOCS 1998, 75, 887.
15. Renner, A.; Cotting, J. A. J Appl Polym Sci 1990, 39, 789.
16. Ustamehmetoğlu, B.; Kızılcan, N.; Saraç, S.; Akar, A. J Appl Polym Sci 2001, 82, 1098.
17. Kızılcan, N.; Ustamehmetoğlu, B. J Appl Polym Sci 2005, 96, 618.
18. Uyanık, N., Kızılcan, N.; Akar, A. J Appl Polym Sci 1998, 67, 643.
19. Kızılcan, N.; Akar, A. J Appl Polym Sci 2005, 98, 97.
20. Uyanık, N.; Yıldırım, H.; Kızılcan, N.; Akar, A. Angew Macromol Chem 1991, 191, 1.
21. Uyanık, N.; Yalçinkaya, H.; Kızılcan, N. Surf Coat Inter Part B: Coat Trans 2001, 84 B4, 243.

22. Kızılcan, N.; Akar, A. J Appl Polym Sci 2002, 85, 500.
23. Kızılcan, N. J Appl Polym Sci 1999, 72, 927.
24. Ergun, S.; Kızılcan, N.; Onen, A. J Appl Polym Sci 2007, 105, 1012.
25. Cakır Canak, T.; Kizilcan, N.; Serhatlı, İ. E. J Appl Polym Sci 2011, 119, 183.
26. Liu, s.; Sen, A. Macromolecules 2000, 33, 5106.
27. Brodeck, M.; Alvarez, F.; Moreno, A.; Colmenero, J.; Richter, D. Macromolecules 2010, 43, 3036.
28. Dupayage, L.; Save, M.; Dellacherie, E., Nouvel, C., Six, J. J Polym Sci Part A: Polym Chem 2008, 46, 7606.
29. Vivek, A. V.; Dhamodharan, R. J Polym Sci Part A: Polym Chem 2007, 45, 3818.
30. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
31. Hawker, C. J.; Hedrick, J. L. Macromolecules 1995, 28, 2993.
32. Benoit, D.; Chaplinski, V.; Brasiau, R.; Hawker, C. J. J Am Chem Soc 1999, 121, 3904.
33. Moad, G.; Rizzardo, E. Macromolecules 1995, 28, 8722.
34. Wang, J. S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614.
35. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 1721.
36. Gaynor, J. S.; Wang, J. S.; Matyjazewski, K. Macromolecules 1995, 28, 8051.
37. Pattern, T. E.; Xia, J. H.; Abernathy, K.; Matjaszewski K. Science 1996, 272, 866.
38. Ashford, E. J.; Naldi, V.; O'Dell, R.; Billingham, A. C.; Armed, S. P. Chem Commun 1999, 1285.
39. Wang, X. S.; Luo, N.; Ying, S. K. Polymer 1999, 40, 4515.
40. Zhang, Z. B.; Ying, S. K.; Shi, Z. Q. Polymer 1999, 40, 5439.
41. Liu, Y.; Wang, L. X.; Pan, C. Y. Macromolecules 1999, 32, 8301.
42. Pattern, T. E.; Matjaszewski, K. Adv Mater 1998, 10, 901.
43. Ishizu, K.; Takahashi, D.; Takeda, H. Macromol Rapid Commun 2000, 21, 660.
44. Fu, G. D.; Phua, S. J.; Kang, E. T.; Neoh, K. G. Macromolecules 2005, 38, 2612.
45. Park, C. W.; Lee, S. J.; Kim, D.; Lee, D. S.; Kim, S. C. J Polym Sci, Part A: Polym Chem 2008, 46, 1954.
46. Nomura, K.; Abdellatif, M. M. Polymer 2010, 51, 1861.
47. Zhong, C. R.; Jiang, L. F.; Peng, X. H. J Polym Sci Part A: Polym Chem 2010, 48, 1241.
48. Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. Prog Polym Sci 2008, 33, 759.
49. Kızılcan, N.; Akar, A. J Appl Polym Sci 1996, 60, 465.