

Graft Copolymerization of Methyl Methacrylate with an *N*-Substituted Maleimide–Liquid-Crystalline Copolymer by Atom Transfer Radical Polymerization

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ABSTRACT: The synthesis of novel copolymers consisting of a side-group liquid-crystalline backbone and poly(methyl methacrylate) grafts were realized by the use of atom transfer radical polymerization (ATRP). In the first stage, the bromine-functional copolymers 6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate and (2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate were synthesized by free-radical polymerization. These copolymers were used as initiators in the ATRP of methyl methacrylate to yield graft copolymers. Both the macroinitiator and graft copolymers were characterized by ¹H-NMR, gel per-

meation chromatography, differential scanning calorimetry, and thermogravimetric analysis. The ATRP graft copolymerization was supported by an increase in the molecular weight of the graft copolymers compared to that of the macroinitiator and also by their monomodal molecular weight distribution. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2074–2081, 2008

Key words: atom transfer radical polymerization (ATRP); graft copolymers; high performance polymers; liquid-crystalline polymers (LCP)

INTRODUCTION

Block and graft copolymers rank among the most interesting tailor-made polymer products because they combine the properties of several different homopolymers in a single molecule.¹ Because of the presence of a covalent bond between each segment, these type of copolymers lead to well-organized nanoscale morphologies both in bulk and in solution. Block and graft copolymers are used for a variety of applications, including impact-resistant materials, thermoplastic elastomers, compatibilizers, polymeric emulsifiers, membranes, and drug-delivery systems. The possibility of the design of optimal material properties through the use of appropriate graft or block structures suggests tremendous commercial potential, and both block and graft copolymers have achieved considerable industrial importance.

Atom transfer radical polymerization (ATRP), a very recent method of controlled polymerization, has already been widely used for the synthesis of block, graft, and star copolymers and polymers with more complex structures based on polymethacrylates, polystyrene (polySt), and their copolymers.^{2–8} Graft copolymers have been prepared by ATRP, with vari-

ous approaches such as grafting through or grafting from.^{9–11} The grafting-through approach includes the synthesis of a well-defined macromer by ATRP in the first step followed by its free-radical or controlled radical copolymerization with a low-molecular-weight monomer. In the grafting-from approach, a polymer having ATRP-functional halide atoms as side groups can be used as a macroinitiator in the ATRP of a second monomer. The combination of ATRP and grafting allows the control of the main-chain parameters [degree of polymerization (DP) and weight-average molecular weight (M_w)/number-average molecular weight (M_n)] and the predetermination of side-chain density and side-chain distribution. This method is not restricted to linear macroinitiators; particles^{12,13} and surfaces^{10,11} can also be functionalized and used as macroinitiators to obtain inorganic organic hybrid materials. These strategies have led to graft copolymers with controlled polydispersities, functionalities, copolymer compositions, backbone lengths, branch lengths, and branch spacings.^{14–16}

In recent years, *N*-substituted maleimide (MI) monomers, such as *N*-phenylmaleimide and *N*-hydroxyphenylmaleimide have become important as they contain a rigid planar ring and can effectively enhance the glass-transition temperature (T_g) and degradation temperature of copolymers.^{17,18} The incorporation of *N*-substituted maleimides into polymer chains, as in thermoplastic resins, improves the heat resistance, solvent resistance, chemical stability, and

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other properties of these materials. The copolymerization of maleimides have been studied extensively to prepare copolymers with better properties. Because of the feasibility of their radical polymerization and the excellent thermal stability of the resultant polymers, many interesting compounds have been attached to them, and their homopolymerization and copolymerization have been studied extensively.^{19–21}

However, the homopolymerization of maleimides has not received much attention because of their symmetrically substituted and steric hindered C=C double bonds. The alternating copolymerizations of MI monomers with electron-rich monomers have also been reported recently.^{22,23} The presence of MI moieties result in low backbone flexibility and, consequently, a high T_g .

The synthesis of copolymers containing amorphous and liquid-crystalline (LC) segments are also popular and can originate a vast number of possible combinations of properties and structures.^{24–34} The molecular design and synthesis of LC polymers, especially LC block or graft copolymers, toward well-defined polymer nanoarchitectures have captured considerable attention. Copolymers with both LC properties and phase-separation properties offer unique opportunities to manipulate LC order in nanometer scales.^{35–37}

This article discusses the synthesis of graft polymers, which combine the properties of different structures in a single macromolecule. For this purpose, poly[6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate]-*alt*-polymaleimide macroinitiators, containing ATRP functional halide groups were prepared by the free-radical copolymerization of *N*-substituted bromomaleimide and 6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate (LC6). These macroinitiators were then used in the graft copolymerization of methyl methacrylate (MMA). The obtained copolymers were characterized with ¹H-NMR, Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) methods.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF; J. T. Baker Inc., Phillipsburg, NJ) was dried over potassium hydroxide and distilled over CaH₂. Dimethyl sulfoxide (Merck & Co., Inc., Whitehouse Station, NJ) was refluxed over CaH₂ and distilled under reduced pressure (76°C and 12 mmHg). Chloroform (J. T. Baker) was shaken with several portions of concentrated H₂SO₄, washed thoroughly with water, and dried with CaCl₂ before it was filtered and distilled (61°C and 760 mmHg). LC6 was prepared according to a literature procedure.³⁸ MMA (Fluka-Aldrich Co., Seelze, Germany) was purified by conventional methods and distilled

in vacuo over CaH₂ just before use. Other chemicals, including MI (Aldrich Co., St. Louis, MO), *N,N,N',N'',N'''*-pentamethyl-diethyl-diethylenetriamine (PMDETA; Aldrich), acryloyl chloride (Aldrich), copper(I) bromide (Aldrich), formaldehyde (Acros Co., Geel, Belgium), anisole (Acros), triethylamine (Acros), and 2-bromopropionyl bromide (Aldrich), were used without further purification. *N*-Methylol-maleimide (NMM) was prepared according to the modified method of Tawney et al.³⁹

Synthesis of (2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate (MBr)

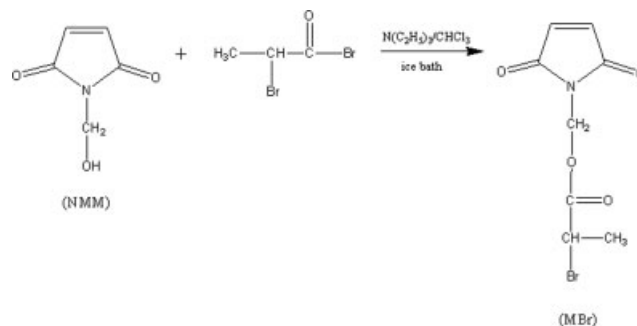
Under nitrogen, 6.24 mL (0.059 mol) of 2-bromopropionyl bromide was added dropwise to a stirring mixture of NMM (6 g, 0.047 mol) and triethylamine (8.22 mL, 0.058 mol) in 140 mL of CHCl₃ in an ice bath for 1 h. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 h. The reaction mixture was washed with water (3 × 140 mL) and then dried over MgSO₄. After filtration and the evaporation of CHCl₃, a greasy dark red product was obtained. It was dried *in vacuo* and recrystallized from ethanol.

mp: 68–71°C. Yield: 47%. ¹H-NMR (CDCl₃, δ, ppm): 4.2–4.3 (m, 1H), 1.6–1.8 (d, 3H), 5.5–5.6 (m, 2H), 6.8 (s, 2H). FTIR (KBr, ν, cm⁻¹): 1720 (C=O of ester stretching), 1419 (C–N), 694 (C–Br).

ANAL. (262 g/mol). Calcd: C, 36.64%; H, 3.05%; N, 5.34%. Found: C, 36.22%; H, 2.98%; N, 4.95%.

Synthesis of the poly[(2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate]-*alt*-poly[6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate] [poly(MBr)-*alt*-poly(LC6)] macroinitiators

To a Schlenk tube equipped with a magnetic stirrer, vacuum and dry nitrogen was applied three or four times; then, certain amounts of monomers (LC6 and MBr), initiator, 2,2'-azobisisobutyronitrile (AIBN), and toluene were introduced under nitrogen. The flask was sealed and then immersed in an oil bath held by a thermostat at 70°C. At the end of the given



Scheme 1 Synthesis of MBr.

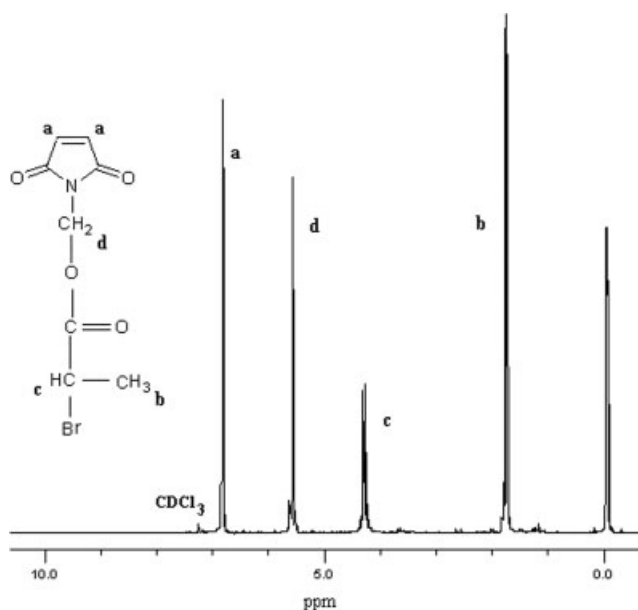


Figure 1 $^1\text{H-NMR}$ spectrum of MBr.

reaction time, the copolymers were obtained from the reaction mixture by precipitation into methanol and were dried. The polymers were purified by reprecipitation from the THF solution into excess methanol and were then dried *in vacuo* for several hours.

Synthesis of graft copolymers of MMA by ATRP

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, bipyridine, and the macroinitiator poly(MBr)-*alt*-poly(LC6) were added in the order mentioned under nitrogen. The reaction solution was bubbled by nitrogen to remove dissolved gases, and then, the tube was immersed in an oil bath and held by a

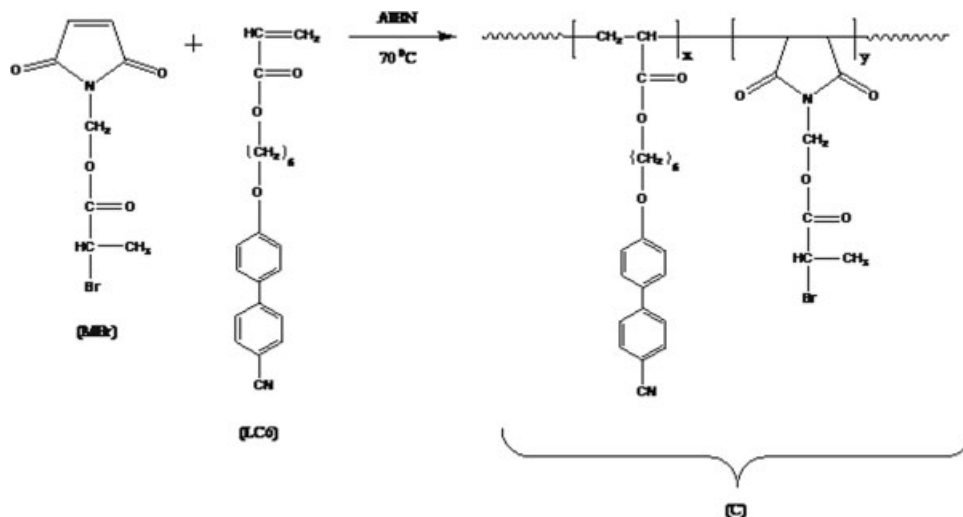
thermostat at 90°C with rigorous stirring. The polymerization was performed for a determined time. Then, the tube was cooled to room temperature, and the contents were dissolved in large amount of THF. The THF solution was passed through a short neutral alumina column to remove copper complex, and then, excess THF was removed by evaporation. The polymer was precipitated into excess methanol, isolated by vacuum filtration, and dried at room temperature *in vacuo* for 24 h. The conversion was determined gravimetrically.

Analysis and characterization

GPC analyses were carried out with a setup consisting of an Agilent pump and a refractive-index detector (model 1100) and four Zorbax PSM (1000S, 300S, 60S) columns (Agilent Co., Santa Clara, CA). THF was used as the eluent at a flow rate of 0.5 mL/min at 30°C . The molecular weights of the polymers were calculated with the aid of poly(St) standards (Varian Inc., Palo Alto, CA). FTIR was measured with a Jasco model FTIR-5300 spectrometer (Jasco Inc., Tokyo, Japan). $^1\text{H-NMR}$ analysis were recorded on a Bruker 250-MHz spectrometer (Bruker Inc., Madison, WI) with CDCl_3 as the solvent and tetramethylsilane as the internal standard. The thermal properties of the copolymers were measured by DSC (TA, DSC Q10) (TA Instruments Inc., New Castle, DE) in a flowing nitrogen atmosphere at scanning rate of $10^\circ\text{C}/\text{min}$. The thermal stability of the copolymers was measured by thermogravimetric analysis (TGA; TA, TGA Q50) in a flowing nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

In this study, graft copolymers of MMA with *N*-substituted MI-LC6 copolymers were synthesized via a



Scheme 2 Synthesis of poly(MBr)-*alt*-poly(LC6).

TABLE I
Copolymerization of LC6 and MBr at 70°C

Run ^a	Time (h)	Conversion (%)	M_n^b	M_n^c	M_w/M_n^b	MBr (mol %) ^b
C1	14	21	12,100	32,494	1.56	28
C2	80	44	12,500	31,707	1.65	37
C3	96	59	13,000	31,358	2.06	40
C4	144	42	13,200	31,270	1.67	45

^a [LC6] = [MBr] = 0.5 mol/L for the synthesis of C1, C2, and C3; [LC6] = [MBr] = 0.6 mol/L for the synthesis of C4; [AIBN] = 0.01[LC6] = 0.01[MBr].

^b Determined from GPC based on PSt standards.

^c Determined from ¹H-NMR spectrum.

two-step procedure involving free-radical polymerization (FRP) and ATRP. For this purpose, a functional initiator having bromine groups was synthesized by the esterification of the NMM with 2-bromopropionyl bromide, as reported previously²³ (Scheme 1).

The structure of the product (MBr) was confirmed by spectroscopic investigations. The ¹H-NMR spectrum recorded in CDCl₃ evidenced resonance signals of —CH₃, —CH₂, —OCH₂, and monomeric MI, with protons of relative intensities corresponding to the number and type of protons (Fig. 1). The FTIR spectrum of MBr also indicated no signal corresponding to —OH groups of the starting NMM and gave the characteristic CO ester band at 1720 cm⁻¹.

In the first stage, MBr was copolymerized with LC6 monomer in the presence of AIBN at 70°C to obtain alternating copolymers with one reactive bromine group in every repeating unit. In the second stage, bromine functional polymers were used as an initiator in the ATRP of MMA to obtain graft copolymers.

Synthesis of alternating copolymers of LC6 and MBr by the FRP mechanism

LC6 and MI represent a monomer pair with a strong tendency toward radical alternating copolymerization. The copolymerization of these monomers proceeded much faster than their homopolymerization when LC6 and MBr were copolymerized according to FRP in the presence of AIBN as an initiator (Scheme 2). Typical results concerning the copolymerization of LC6 with MBr are presented in Table I.

The ¹H-NMR spectrum (Fig. 2) of a typical alternating copolymer displays signals at 2.34 ppm (CH of LC6), 3.73–3.76 ppm (MI ring protons, CH), 3.92–4.07 ppm (O—CH₂ of LC6), 4.31 ppm (—CH—Br), 5.52 ppm (O—CH₂ of MI), and 6.91–7.59 ppm (CH of LC6 aromatic rings). To determine the copolymer composition, the ratio of integral intensities of imide protons to LC6 aromatic protons was used. MBr molar fraction in the copolymer was obtained with the following equation:

$$\text{MBr (mol \%)} = [A_1 / (A_1 + A_2)] \times 100\%$$

where MBr (mol %) is the molar fraction of maleimide in the copolymer, A_1 is the integrated area for

one proton in the maleimide unit, and A_2 is the integrated area for one aromatic proton in the LC6 unit.

M_n and M_w/M_n data obtained for the copolymers investigated are also included in Table I. The calibration was made with PSt standards, and no consideration for the difference in nature between the copolymers and PSt was given. These molecular weight values should thus be taken as a relative comparison between the different copolymers and not as absolute values. Table I shows that the MBr fraction of the copolymer increased with the polymerization time. All polymers had a lower MBr fraction than perfectly alternating copolymers, which would have had an MBr fraction of 0.5. However, the copolymerization of MI and acrylates has a tendency toward alteration that has already been observed kinetically for the radically initiated copolymerization of such monomers.^{40–42}

Synthesis of the graft copolymers

It is well known that 2-bromopropionyl bromide is an excellent initiator for ATRP of styrene and acrylates with a high initiating efficiency.² Therefore, alternating copolymers having 2-bromopropionyl functionality on the MI segments were synthesized

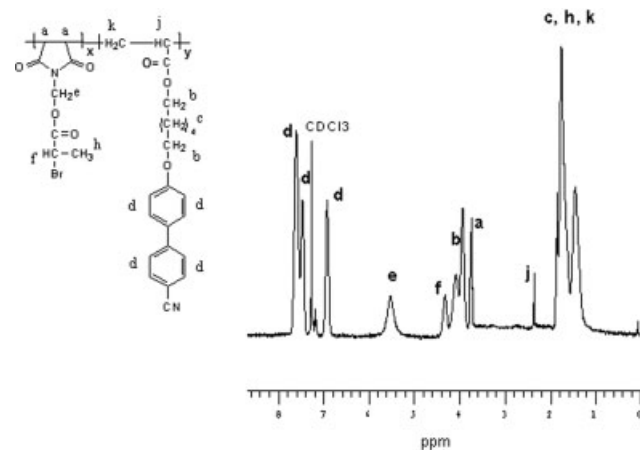
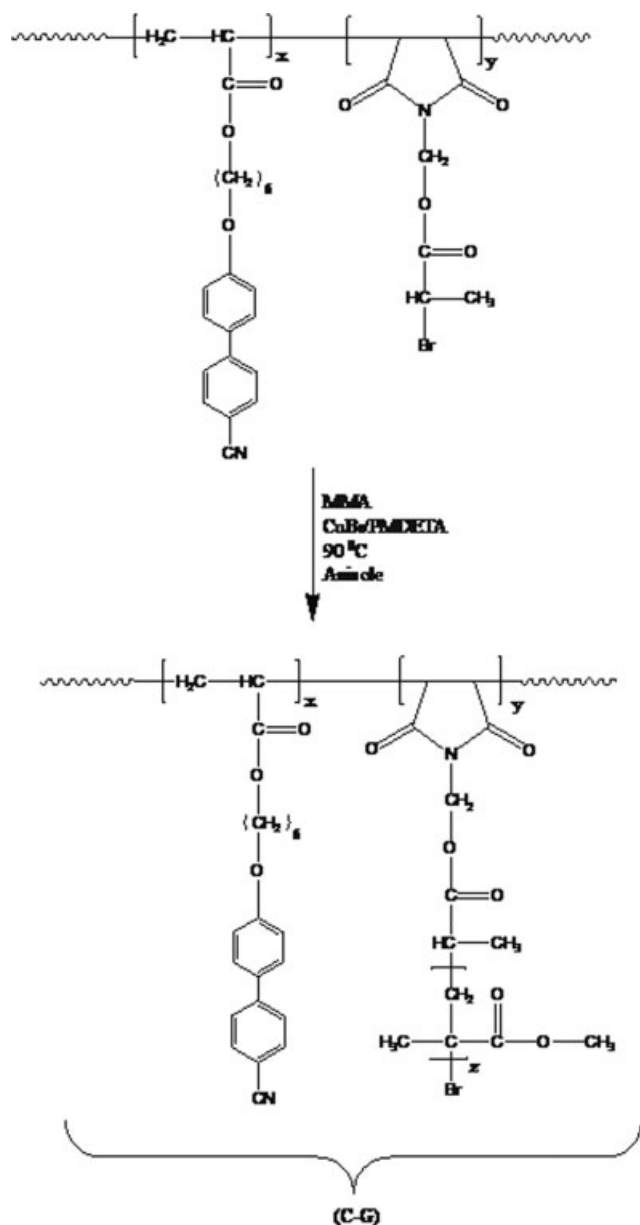


Figure 2 ¹H-NMR spectrum of poly(MBr)-alt-poly(LC6).



Scheme 3 Synthesis of [poly(MBr)-*alt*-poly(LC6)]-*g*-poly(MMA).

and used as macroinitiators to initiate the ATRP of MMA to prepare graft copolymers, as mentioned previously (Scheme 3).

The graft 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 Table II. M_n and the polydispersity of the macroinitiator C3 determined by GPC were 13,000 and 2.06, respectively, and those for the macroinitiator C4 were 13,200 and 1.67, respectively.

During the graft copolymerization of C3 with MMA for 12, 24, and 48 h with the same ratios of macroinitiators, the average molecular weights increased to 61,000, 97,000, and 145,000, respectively, whereas the polydispersity values decreased to 1.47, 1.43, and 1.40, respectively. These results were also in good agreement with the MMA percentage of the graft copolymers. Similar behavior was also observed in the graft copolymerization of C4 with MMA. As also shown in Table II, the molecular weights of the resulting copolymers increased with the conversion because of the living character of the investigated free-radical copolymerization.

The GPC traces of the macroinitiators and corresponding graft copolymers obtained at different reaction times are shown in Figure 3. The molecular weights obviously shifted to a higher molecular weight region with monomodal distribution, which indicated that almost all of the macroinitiators were converted to graft copolymers. The [poly(MBr)-*alt*-poly(LC6)]-*g*-poly(MMA) copolymers were also characterized by FTIR and $^1\text{H-NMR}$ spectroscopy. The FTIR spectrum of the graft copolymer displayed a carbonyl stretch (1730 cm^{-1}) related to carbonyl groups of both the PMMA segments and MI segments.

The $^1\text{H-NMR}$ spectrum indicated the presence of OCH_3 protons at 3.58 ppm in addition to characteristic signals of poly[(2,5-dioxo-2,5-dihydro-1*H*-pyrrole-1-yl)methyl 2-bromopropanoate] and poly[6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate] segments of alter-

TABLE II
Graft Copolymerization by ATRP at 90°C^a

Run ^a	Time (h)	Conversion (%)	M_n^b	$M_{n(\text{NMR})}^c$	$M_{n(\text{theo})}^d$	M_w/M_n^b	MMA graft (mol %) ^e
C3-G1	12	25.0	61,000	154,000	62,700	1.47	55
C3-G2	24	37.0	97,000	89,800	86,700	1.43	60
C3-G3	48	45.0	145,000	195,800	102,800	1.40	73
C4-G1	24	29.0	38,000	56,700	71,000	1.14	10
C4-G2	48	32.5	40,000	60,000	78,000	1.10	27

^a $[\text{I}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0/[\text{MMA}]_0 = 1 : 2 : 4 : 2000$; $[\text{MMA}] = 3.9\text{ mol/L}$.

^b Determined from GPC on the basis of polySt standards.

^c Calculated from the $M_{n(\text{NMR})}$ equation.⁴⁰

^d Calculated from $M_{n(\text{theo})} = [(M_0/I_0) \times (\% \text{ conversion}) \times M_w \text{ monomer}] + M_n \text{ macroinitiator}$. $M_{n(\text{theo})}$, theoretical molecular weight of graft copolymers; $[M]_0$, molar concentration of monomer; $[I]_0$, molar concentration of initiator; $M_n \text{ macroinitiator}$, molecular weight of macroinitiator by GPC; $M_w \text{ monomer}$, molecular weight of monomer, MMA.

^e Calculated from $^1\text{H-NMR}$.

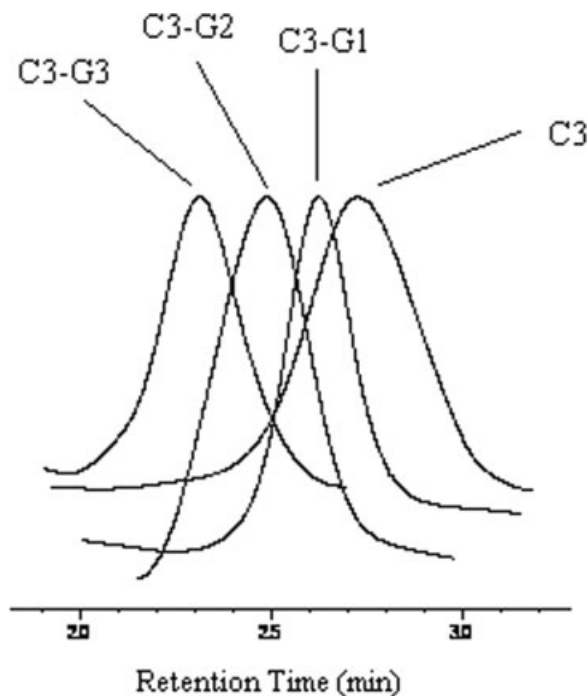


Figure 3 GPC traces of C3, C3-G1, C3-G2, and C3-G3.

nating copolymers. Signals due to the CH—Br protons ($\delta = 4.1$ ppm) of the macroinitiator were also shifted to $\delta = 2.0$ ppm, which indicated the consumption of bromine in the ATRP of MMA (Fig. 4).

$M_{n(\text{NMR})}$, defined as molecular weight of polymers based on NMR results, were calculated from the $^1\text{H-NMR}$ spectrum, according to the following equation:⁴³

$$M_{n(\text{NMR})} = M_{n(\text{first polymer})} \left(1 + X \frac{\text{MW}_{\text{second monomer}}}{\text{MW}_{\text{first monomer}}} \right) + Y M_{n(\text{first polymer})}$$

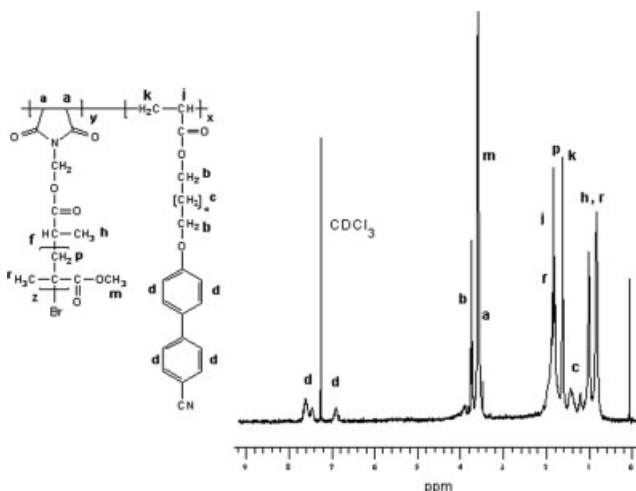


Figure 4 $^1\text{H-NMR}$ spectrum of [poly(MBr)-*alt*-poly(LC6)]-*g*-MMA.

TABLE III
DSC and TGA Data for the Precursor Polymers and Graft Copolymers

Polymer	T_g ($^{\circ}\text{C}$) ^a	$T_{50\%}$ ($^{\circ}\text{C}$) ^b	Residue at 500 $^{\circ}\text{C}$ (%) ^b	T_{N-I} ($^{\circ}\text{C}$) ^c
C3	59	338.00	18.75	115
C3-G1	107	394.87	1.48	nd
C3-G2	112	390.63	1.42	nd
C3-G3	118	388.05	1.26	nd
C4	59	355.99	21.00	115
C4-G1	108	387.90	2.20	nd
C4-G2	110	392.20	1.60	nd

nd = not detected.

^a Detected by DSC.

^b Detected by TGA.

^c Observed by polarizing optical microscopy.

where $M_{n(\text{first polymer})}$ is molecular weight of initiating macromolecule, $\text{MW}_{\text{second monomer}}$ is molecular weight of MMA, $\text{MW}_{\text{first monomer}}$ is molecular weight of LC6, X is the molar ratio of the second monomer units to the first monomer units in the copolymer as measured by $^1\text{H-NMR}$, and Y is the percentage of maleimide units in the alternating copolymer as measured by $^1\text{H-NMR}$. The $M_{n(\text{first polymer})}$ value was based on the apparent MW of poly(MBr)-*alt*-poly(LC6) estimated by GPC with PSt standards. The calculated values are presented in Table II.

The thermal and LC properties of polymers were checked with DSC, TGA, and polarizing optical microscopy measurements. The results of thermal analysis are summarized in Table III and Figures 5 and 6. In the DSC thermograms (heating), we observed two endothermic events; one occurring at a lower temperature (59 $^{\circ}\text{C}$), as a shift of the baseline toward the endothermic direction was due to the T_g of the polymers, and the other corresponded to the nematic-to-isotropic phase-transition temperature (T_{N-I}) of the polymer liquid crystals. The introduction of MI units into common vinyl polymers or LC poly-

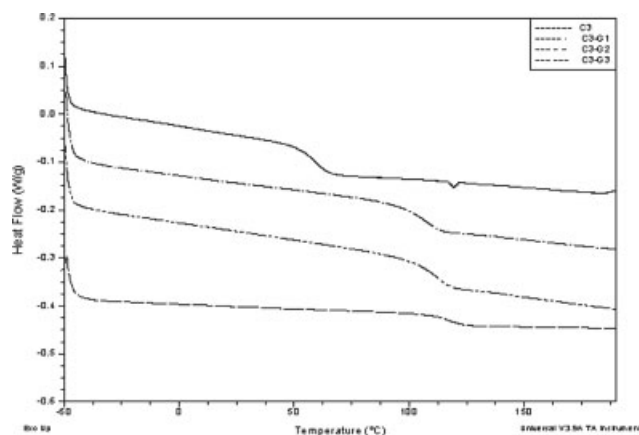


Figure 5 DSC thermograms of C3, C3-G1, C3-G2, and C3-G3.

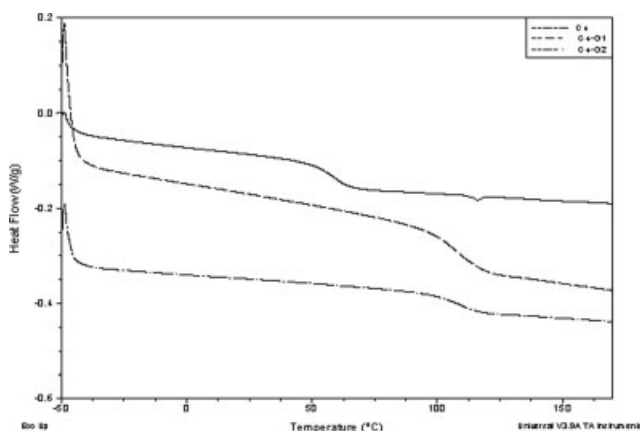


Figure 6 DSC thermograms of C4, C4-G1, and C4-G2.

mers was expected to improve their thermal stability because of the incorporation of rigid polar MI units into the backbone. Normally, T_g values of LC segments give an endothermic peak at 30°C; in our case, T_g values increased up to 59°C due to the effect of the rigidity of MI units and their ability to form hydrogen bonds. The pendant groups increased separation of the polymer chains and introduced more free volume, which thus resulted in a much lower T_g value compared to polymaleimide itself. Extending the length of the spacer group of the second monomer, such as the LC part containing six methylenic units, also resulted in a further decrease (59°C) in T_g due to the increased plasticizing effect of the spacers.

The mesogenic properties were compared to those of previously explained poly(maleimide-*alt*-styrene) and those of polyacrylates containing similar mesogens.^{23,44} Poly[maleimide-*alt*-6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate] exhibited liquid crystallinity as a nematic mesophase; however, this type of polymer has a more flexible backbone than poly(MI-*alt*-St), and hence, there was a higher degree of decoupling

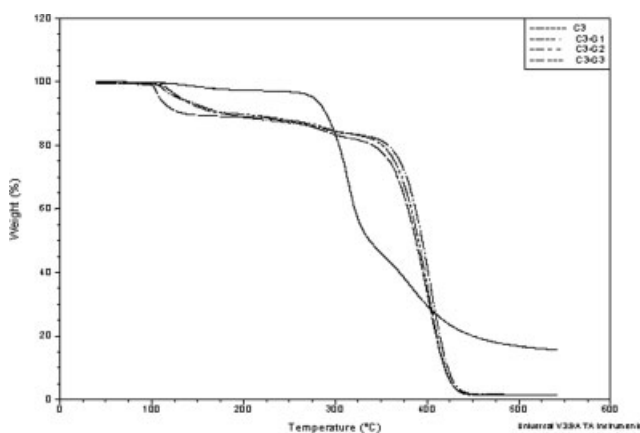


Figure 7 TGA thermograms of C3, C3-G1, C3-G2, and C3-G3.

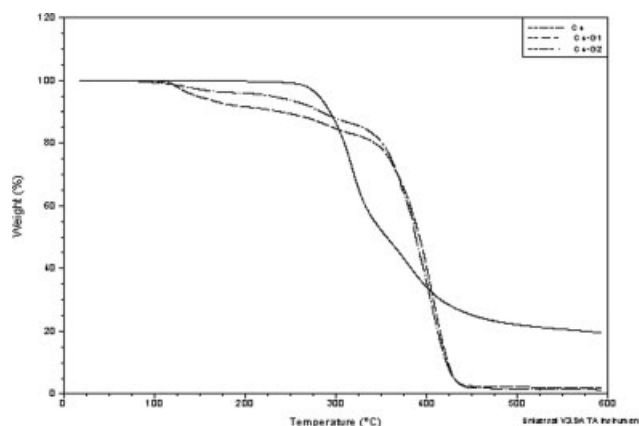


Figure 8 TGA thermograms of C4, C4-G1, and C4-G2.

between the motions of the backbone and those of the mesogens. In our previous study with poly(MI-*alt*-St),²³ conformational changes in the backbone were inherently hindered, which thus resulted in a high T_g value (231°C). The grafting of MMA groups to a polymer backbone will have opposing effects; the bulky MMA groups will severely hinder main-chain motions, slow down the molecular dynamics, and thus increase T_g . Figures 7 and 8 show the TGA curves for the graft copolymers and corresponding precursor copolymers.

The TGA measurements provided a better explanation for the contribution of MI units on thermal stability with respect to the five-membered cyclic structure in the copolymer chain. The 50% weight loss temperature ($T_{50\%}$) was assumed simply as a measurement of thermal stability, and the related results are presented in Table III. All of the selected graft copolymers indicated a higher $T_{50\%}$ relative to their precursor copolymers, and they left residue in a lower ratio than their precursor copolymers due to the much pronounced effect of the rigid MI unit. As shown in Table III, C3, C4, and related copolymers showed good thermal stability. In our case, the graft copolymers showed higher $T_{50\%}$ values than neat PMMA (305.6°C), which indicated that the graft copolymer exhibited a better thermal stability than that of PMMA.⁴⁵

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