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ABA Type Triblock Copolymer Based on Mesogen-Jacketed Liquid Crystalline Polymer: Design, Synthesis, and Potential as Thermoplastic Elastomer

Yi Yi,[†] Xinghe Fan,[†] Xinhua Wan,[†] Lei Li,[†] Ning Zhao,[‡] Xiaofang Chen,[†] Jian Xu,[‡] and Qi-Feng Zhou*[,†]

Department of Polymer Science & Engineering, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China, and State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT: We have designed and successfully prepared a well-defined ABA type triblock copolymer consisting of poly(*n*-butyl acrylate) as soft B block and poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS) as hard A block with potential as liquid crystalline thermoplastic elastomer (LCTPE). The synthetic strategy is to obtain a difunctional poly(*n*-butyl acrylate) first and then use it as a macroinitiator for chain extension. Both steps employ atom transfer radical polymerization (ATRP). Kinetic study of the chain-extension polymerization demonstrates a well-controlled process. The resulted triblock copolymers have high molecular weights ($M_n > 70\,000$) and low molecular weight distributions ($M_w/M_n < 1.2$). Their chemical structures are confirmed by nuclear magnetic resonance. Curves of differential scanning calorimetry indicate the immiscibility of the two components. Morphological investigations were made with transmission electrical microscopy and gave direct evidence of the existence of nanophase-separated structures with long-range order. After examinations by polarized optical microscopy, we found the triblock copolymers are LC only if the molecular weight of PMPCS block exceeds 20 000. Wide-angle X-ray diffraction measurements indicate a very stable nematic phase between glass transition of PMPCS block and decomposition. We found three samples are elastomeric. Preliminary mechanical tests were done on their films. Typical dynamic mechanical analysis and tensile tests prove that the sample has the potential as thermoplastic elastomers (TPEs). According to our best knowledge, the unique triblock copolymer is the first reported well-defined ABA type TPE imparting liquid crystallinity to the hard domains which serve as “physical cross-links”. Since the novel LC block copolymer has the rod−coil−rod conformation, it is also a new type of elastic rod−coil block copolymer.

Introduction

Mesogen-jacketed liquid crystalline polymers (MJLCPs)[1] represent a kind of special polymers which attracted increasing interest in these years. For a MJLCP, the mesogenic pendants are connected laterally to the polymer backbones with no or very short spacers. Therefore, mesogenic pendants are densely packed around the backbone and force it to adopt a semirigid conformation.[2] Just like the side-chain liquid crystalline polymer (SCLCP) with rigid-rod-like poly(*p*-phenylene) as backbone,[3] MJLCPs have unique properties quite different from conventional SCLCPs[4]—the stable LC phase in a broad temperature and the director of LC phase determined by the backbone, not by the mesogenic side groups. As novel materials, MJLCPs are of both academic and practical interest. The most striking one is that we can get polymers having properties like main-chain liquid crystalline polymers (MCLCPs) only through free radical polymerization frequently employed in the synthesis of SCLCPs instead of the demanding condensation polymerization. In particular, with the potential help of controlled radical polymerization (CRP) recently involved in the syntheses of SCLCPs,[5] we can prepare well-defined MJLCPs-based block copolymers having unique thermal and self-assembly behaviors, such as rod−coil block copolymers.[6]

Since the idea of MJLCP was proposed in 1987,[1a] a series of MJLCPs[7] and block copolymers containing MJLCPs[8] were synthesized and studied. They are mostly based on 2,5-disubstituted styrenic LC monomers. Ober et al.[7f] studied stable free radical polymerization (SFRP) kinetics of 2,5-(4-butylbenzoyl)oxystyrene (BBOS). Then they prepared rod−coil block copolymers consisting of polystyrene and poly(2,5-(4-butylbenzoyl)oxystyrene) (PBBOS) with different architectures by SFRP and studied their morphological and rheological behaviors.[8d] In recent years, we focus on the studies of a MJLCP, poly{2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene} (PMPCS). Its monomer, MPCS, is compatible with SFRP[9] and atom transfer radical polymerization (ATRP).[10] We synthesized a series of rod−coil diblock copolymers PS-*b*-PMPCS by SFRP[8a] and then investigated their self-assembly behavior in dilute solutions by laser light scattering (LLS).[11] Furthermore, the supramolecular columnar nematic phase of PMPCS segment of PS-*b*-PMPCS was identified by a combination of wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS).[12] The first hybrid LC rod−coil diblock copolymer, PMPCS-*block*-poly(dimethylsiloxane) (PMPCS-*b*-PDMS), was also prepared by ATRP.[8c] Among the reported block copolymers based on MJLCPs, most of them are diblock copolymers and only one triblock copolymer of PBBOS-*b*-PS-*b*-PBBOS synthesized by SFRP.[8d]

In the present study, we are specifically interested in the synthesis of a linear symmetrical triblock copoly-

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[†] Peking University.

[‡] Institute of Chemistry, CAS.

* Corresponding author. E-mail: qfzhou@pku.edu.cn.

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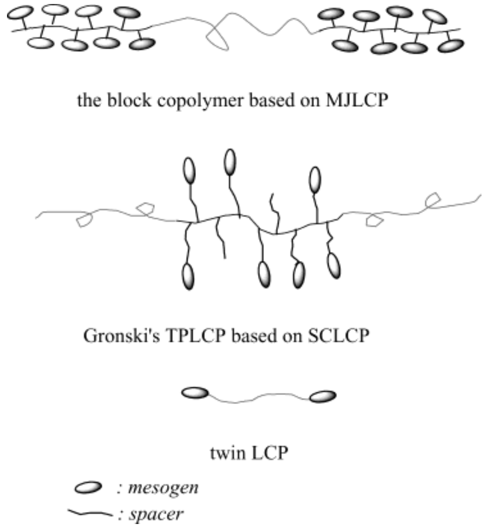
mer (ABA type copolymer) based on MJLCP. As is well-known, ABA type copolymers with a rubbery central B block and hard terminal A blocks have the potential to act as thermoplastic elastomers (TPEs)[13] like the well-known SBS and SIS. TPEs are biphasic polymeric networks: the continuous soft phase provides elastomeric properties, and the discrete hard phase serves as "physical cross-links" which immobilize the soft matrix. If mesogenic units are introduced into the biphasic networks, the ABA type copolymers turn into special liquid crystalline/isotropic (LC/I) block copolymers which can be termed "liquid crystalline thermoplastic elastomer (LCTPE)". LCTPEs combine mechanical and LC properties in the anisotropic networks with the ease of processing. Moreover, as LC/I block copolymers, ABA type LCTPEs provide a good opportunity to investigate the competition between mesomorphic order and microphase separation.[14]

Up to now, there are limited examples of ABA type LCTPEs. Most of them were prepared from anionically polymerized SBS by using a facile method called the "polymer-analogous approach". Gronski et al.[15] did the pioneering work to synthesize such a LCTPE by attaching mesogenic units onto the backbone of a hydroxylated SBS with 100% 1,2-PB content. Zhao et al.[16] prepared similar material by grafting polymerization of LC acrylic monomers onto the central PB backbone of a commercially available SBS. The two obtained triblock copolymers have a common sequence denoted as I/LC/I, which means isotropic hard A-blocks and a side-chain LC B-block. There was only one report of LCTPE with the sequence of LC/I/LC. Ikeda et al.[17] synthesized an elastomeric twin liquid crystalline polymer (TLCP) consisting of a polyolefin oligomer with two terminal mesogenic groups. In the TLCP films, the polar mesogenic groups aggregate and separate into ordered nanodomains which behave as hard blocks. But strictly speaking, it is not a block copolymer. Its mechanical properties are unsatisfying, too. The difficulty to prepare a well-defined ABA type LCTPE having the LC phase as hard domains is that although MCLCPs are suitable for the hard blocks, it is too difficult in a synthetic sense to get such MCLCP-containing triblock copolymers having tailored molecular weights and narrow polydispersities.

Considering its stiff backbones and synthetic way of chain polymerization, PMPCS is a good candidate to act as hard blocks to form a well-defined ABA type TPLCE. It is expected that the new material would have a high service temperature as PMPCS has the glass transition temperature (T_g) around 120 °C. The model of the designed PMPCS-containing triblock copolymer together with those of Gronski's and twin LCPs is presented in Scheme 1 simply for comparison. As MPCS is vulnerable in ionic polymerizations, other synthetic methods must be considered. Enlightened by the synthetic way of a family of fully acrylic TPEs such as poly(methyl methacrylate)-*block*-poly(*n*-butyl acrylate)-*block*-poly(methyl methacrylate) (PMMA-*b*-P*n*BA-*b*-PMMA),[18] polyhedral oligomeric silsesquioxane (POSS)-based block polymer P(MA-POSS)-*b*-P*n*BA-*b*-P(MA-POSS),[19] and poly(octadecyl methacrylate)-*block*-poly(*n*-butyl acrylate)-*block*-poly(octadecyl methacrylate) (POMA-*b*-P*n*BA-*b*-POMA),[20] we design and try to prepare a novel triblock copolymer PMPCS-*b*-P*n*BA-*b*-PMPCS with the potential as LCTPEs by sequential ATRP. The triblock copolymer is the first reported well-defined ABA type TPE having LC "physical cross-links". Moreover, it is also a novel elastic rod−coil block copolymer having narrow polydispersities (M_w/M_n < 1.2) in addition to poly(1-phenylethyl isocyanide)-*b*-polybutadiene-*b*-poly(1-phenylethyl isocyanide) synthesized by nickel catalysis with polydispersities ranging from 2.1 to 3.0.[21]

Scheme 1. Models of ABA Type Copolymers as Liquid Crystalline Thermoplastic Elastomers



Experimental Section

Materials. Diethyl *meso*-2,5-dibromoadipate (DEDBA) (98%, Acros), 1-bromoethylbenzene (BEB) (97%, Acros), and *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (PMDETA) (>98%, TCI) were used without further purification. Copper(I) bromide (Cu^IBr) and copper(I) chloride (Cu^ICl) were purified by stirring in glacial acetic acid, then filtering and washing with ethanol, and then dried under vacuum. Chlorobenzene (Analytical purity, Beijing Chemical Reagents Co.) was treated with powdered CaH_2 and distilled before use. *n*-Butyl acrylate (*n*-BA, 99%) (Acros) was washed with aqueous NaOH solution to remove the inhibitor. After drying over anhydrous magnesium sulfate, it was distilled under reduced pressure.

Characterization. 1. Molecular Weights and Molecular Weight Distributions. The molecular weight distributions (MWDs) of all polymers were measured by size exclusion chromatography (SEC) with a Waters 2410 instrument equipped with three Waters μ-Styragel columns (10^3, 10^4, and 10^5 Å). THF was the mobile phase at the flow rate of 1.0 mL/min at 35 °C. The calibration curve was obtained by PS standards.

The number-averaged molecular weights (M_n) of difunctional P*n*BA macroinitiators were calculated according to the equation

$$\log M_{\mathrm{P}n\mathrm{BA}} = 1.01 \log M_{\mathrm{PS}} - 0.02 \tag{1}$$

which is deduced from Mark−Houwink−Sakurada expression:

$$[\eta] = KM^{\alpha} \Rightarrow \log M = \frac{1}{1+\alpha}[\log([\eta]M) - \log K] \text{ and}$$
$$[\eta]_{\mathrm{P}n\mathrm{BA}} M_{\mathrm{P}n\mathrm{BA}} = [\eta]_{\mathrm{PS}} M_{\mathrm{PS}}$$

with the following viscometric parameters:

$$[\eta] = 1.14 \times 10^{-4} {M_{\mathrm{PS}}}^{0.716} \text{ (PS in THF)}$$

$$[\eta] = 1.22 \times 10^{-4} {M_{\mathrm{P}n\mathrm{BA}}}^{0.700} \text{ (P}n\text{BA in THF)}^{22}$$

The M_ns of triblock copolymers were estimated from their ^{1}H NMR spectra ($CDCl_3$, TMS as internal reference) recorded on

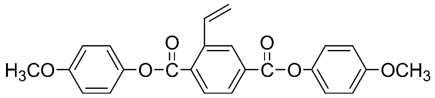


Figure 1. Molecular formula of MPCS.

a Bruker ARX 400 MHz spectrometer based on the calculated M_ns of macroinitiators according to eq 1.

2. Sample Preparation. Transparent thin films of the triblock copolymers were cast from 15 wt % chlorobenzene solutions at room temperature. The solvent was slowly evaporated for about 2 weeks. Then the films were vacuum-dried to eliminate residual solvent. The thickness of the films was about 1 mm.

3. Thermal Analysis. Glass transitions of polymers were investigated by differential scanning calorimetry (DSC) on a TA Instruments Q100 in a temperature range from −90 to 200 °C at a heating rate of 10 °C/min under continuous nitrogen flow. *n*-Octane (mp 56.76 °C) and indium (mp 156.78 °C) were used to calibrate the instrument. The average sample size was about 5 mg, and the nitrogen flow rate was 15 mL/min. A TA Instruments SDT 2960 was used for thermogravimetric analysis of block copolymer samples. Generally, about 3 mg of sample was heated from 50 to 800 °C at a heating rate of 20 °C/min under nitrogen.

4. Liquid Crystallinity Studies. A Leitz Laborlux 12 polarizing optical microscope (POM) with a Leitz hot stage was used to characterize the liquid crystalline behaviors of the triblock copolymers. Wide-angle X-ray diffraction (WAXD) examination was conducted with a Bruker GADDS D8 discover X-ray diffractomer at elevated temperatures. Samples were scanned in a 2θ range between 2° and 30°.

5. Morphology. The microphase separation of sample triD was observed by TEM. Ultrathin sections were cut from a thin film on a cryoultramicrotome. To enhance the electron density contrast between the LC and P*n*BA phases, the sections were stained by RuO_4 vapor at room temperature for 20 min. TEM studies were performed on a Hitachi H-800 electron microscope.

6. Dynamic Mechanical Analysis. A Rheometric Scientific DMTA V was used in the shear mode. The measurements were carried out in sandwich geometry. The disk samples with 11 mm diameter and 1 mm thickness were cut from solution-cast films. Temperature sweep experiments were carried at 1 Hz and a heating rate of 3 °C/min.

7. Tensile Measurements. Tensile tests were performed on an Instron 5567 tester. Microdumbbells of sample triD were cut from solution-cast films and drawn at room temperature at a stretching rate of 100 mm/min.

Synthetic Procedures. 1. Liquid Crystalline Monomer MPCS. The monomer 2,5-bis[(4-methoxyphenyl)oxycarbonyl]-styrene (MPCS) was synthesized from vinylterephthalic acid and 4-methoxyphenol via phosphorylation reaction as previously described.[7c] Its chemical formula is presented in Figure 1.

^{1}H NMR ($CDCl_3$) (δ, ppm): 3.84 (d, 6H, 2 × Ar−OCH_3), 5.47−5.51 (dd, 1H, $-CH{=}CHH$), 5.81−5.87 (dd, 1H, $-CH{=}CHH$), 6.95−7.18 (m, 8H, 2 × CH_3O-Ar-), 7.50−7.60 (q, 1H, $-CH{=}CH_2$), 8.15−8.44 (3H, $CH_2{=}CH-Ar-$). Anal. Calcd for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.32; H, 4.93. Phase transition: K 109 N 144 I.

2. Difunctional Macroinitiators. As an example for macroinitiator C, DEDBA (33.0 mg, 0.1 mmol), $Cu^{I}Br$ (14.4 mg, 0.1 mmol), PMDETA (20.8 μL, 0.1 mmol), and deoxygenated *n*-BA (10 mL, 70 mmol) were successively introduced into a 50 mL reaction tube. After three freeze−pump−thaw cycles, the tube was sealed under vacuum and inserted into a thermostated oil bath at 80 °C. After the polymerization was terminated by putting the tube into ice/water mixture, the tube was broken. The product was then diluted with 300 mL of THF and passed through a basic alumina column to remove copper complex. Then, the polymer solution was concentrated and precipitated into cold methanol. The precipitate was collected and dried in vacuo.

3. Kinetic Studies of Polymerization Initiated with Difunctional Macroinitiators. $Cu^{I}Cl$ (2 mg, 0.02 mmol), MPCS (0.5 g, 1.24 mmol), and PMDETA (3 μL, 0.02 mmol) were placed into a 10 mL reaction tube. Then, 2 mL of chlorobenzene solution of difunctional macroinitiator (0.2 g, $M_n = 22\,800$, $M_w/M_n = 1.20$) was quickly introduced with a syringe. After they were sealed under vacuum, the tubes were put into a 110 °C oil bath. The tubes were broken periodically. Purified block copolymers were obtained by column chromatography using dichloromethane as eluant to eliminate residual monomer. Monomer conversion was measured by gravimetry. SEC was used to determine M_ns and polydispersities of the block copolymers.

4. Triblock Copolymers Initiated with Macroinitiator A, B, or C. Typically, the amount of macroinitiator is 0.6 g. The monomer is added at different concentration according to the designed molecular weight. The polymerization and purification procedure are the same as in section 3.

5. Triblock Copolymer Initiated with Macroinitiator D. For the synthesis of triD, 5.5 g of difunctional macroinitiator D (0.06 mmol) was dissolved in about 30 mL of dichloromethane and then added into a 250 mL Schlenk flask fitted with a rubber septum. After the solvent was totally distilled away under reduced pressure, $Cu^{I}Cl$ (12 mg, 0.12 mmol) and MPCS (4.5 g, 11.13 mmol) were added into the flask. The flask was evacuated and followed by backfilling with nitrogen for three cycles. 50 mL of chlorobenzene being purged with nitrogen for 1 h was transferred into the flask with a syringe. Then, the flask was placed into an oil bath set at 110 °C. After the reaction mixture was kept stirring for 5 min, PMDETA (25 μL, 0.13 mmol) was added with a microinjector through the rubber septum. The system was then homogeneous, and polymerization began at the same time. The process was monitored by syringe sampling. The following procedures of purification were the same as mentioned in section 3.

Results and Discussion

Synthesis. We followed a two-step ATRP strategy pioneered by Jerome et al.[18a] in the synthesis of PMMA-*b*-P*n*BA-*b*-PMMA, except a change in catalytic complex. In Jerome's method, $NiBr_2(PPh_3)_2$ was the only catalyst through the whole polymerization procedures. It worked well for the first step polymerization of *n*-BA but lost good control over the second step polymerization of MMA. According to the bimodal SEC curves at least up to about 30% conversion of MMA, the size of outer PMMA blocks is broadly distributed, which leads to the increase of polydispersity of the triblock copolymer from 1.1 to 1.4. As a result, undesired effects of the attained PMMA-*b*-P*n*BA-*b*-PMMA such as poor mechanical properties were observed. Later, an improvement of molecular weight distributions of terminal PMMA blocks was achieved by replacing $NiBr_2(PPh_3)_2$ with $Cu^{I}Cl/CuCl_2$/dNBipy by Jerome et al.[18d]

In this case, the first step polymerization of *n*-BA was catalyzed by $Cu^{I}Br$/PMDETA in bulk instead of $NiBr_2(PPh_3)_2$ in toluene solution. It is because that the copper complex is cheaper and catalyzes a fast and well-controlled polymerization of *n*BA compared with $NiBr_2(PPh_3)_2$. After isolation and purification, the P*n*BA macroinitiator triggered the polymerization of MPCS in chlorobenzene, a good solvent for both P*n*BA and PMPCS (see Scheme 2). We synthesized several P*n*BA macroinitiators with different M_ns. Their specifications are presented in Table 1.In a former study, our group realized copper-mediated living radical polymerization of MPCS with the ligand of sparteine.[23] As a chiral compound, sparteine is used to mediate stereochemical environment of organic reactions. The choice of sparteine as ligand was based on the assumption that its chirality will favor the formation of optically active helical

Scheme 2. Synthetic Strategy of the Designed ABA Type Triblock Copolymer Based on MJLCP

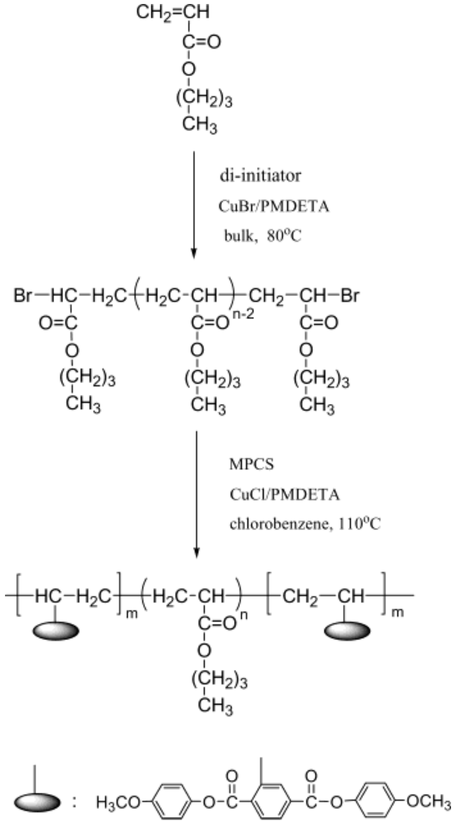


Table 1. Difunctional Macroinitiators Prepared by Bulk ATRP[a]

sample	$[n\text{-BA}]_0$/ $[\text{DEDBA}]_0$	conv (%)	M_n theory[b]	M_n SEC[c]	M_n calcd[d]	M_w/M_n
A	700	49	44K	43K	46K	1.08
B	750	85	83K	79K	84K	1.09
C	700	75	67K	63K	67K	1.10
D	750	95	87K	85K	93K	1.11

[a] Conditions: $T = 80$ °C, bulk polymerization, [DEDBA]:[PMDETA]:[CuBr] = 1:2:2. [b] $M_n(\text{calcd}) = ([n\text{-BA}]_0/[\text{DEDBA}]_0) \times \text{conv} \times 128.17$. [c] Calibrated by PS standards. [d] Calculated according to the calibration equation: $\log M_{\text{P}n\text{BA}} = 1.01 \log M_{\text{PS}} - 0.02$.

polymers, whereas the results were disappointing. So more accessible and more tunable PMDETA was considered in this study. To ensure that the polymerization of MPCS proceeds in a more controlled manner, the technique of halogen exchange[24] was adopted by using Cu$^{\text{I}}$Cl/PMDETA as catalyst.

Kinetic Study of Block Copolymerization. As mentioned above, the catalytic system has tremendous effects on the structures and ultimate mechanical properties of triblock copolymers. If the initiation of macroinitiator and the propagation of monomer were not concerted, bimodal SEC curves would occur during polymerization and lead to low blocking efficiency. To investigate the living character and the efficiency of polymerization, a kinetic study of the polymerization of MPCS was conducted with a dibromo-terminated PnBA having M_n of 22 800 measured by SEC.

The block copolymerization was carried out in chlorobenzene at 110 °C. It proceeded in a homogeneous way. The linear dependence of $\ln([M]_0/[M])$ vs time of the plot in Figure 2 indicates that the polymerization is first order with respect to monomer concentration, and the number of active species remains constant throughout the polymerization. The molecular weight increases linearly with the increase of monomer conversion, and the polydispersity remains narrow (see Figure 3). The corresponding SEC curves at different conversions up to 45% shown in Figure 4 are all symmetrically monomodal and narrow. It illuminates a well-controlled polymerization with high blocking efficiency regulated by Cu$^{\text{I}}$Cl/PMDETA.

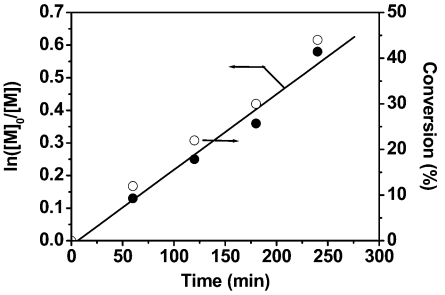


Figure 2. Kinetic plots of time dependence of monomer conversion and $\ln([M]_0/[M])$. Conditions: $T = 110$ °C; solvent: chlorobenzene; $[\text{MPCS}]_0 = 0.62$ M; $[\text{macroinitiator}]_0 = 4.39$ mM; [CuCl]/[PMDETA] = 1.

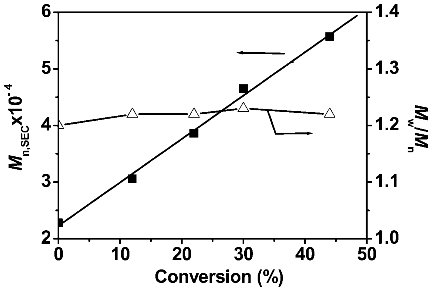


Figure 3. Dependence of molecular weight and molecular weight distribution by SEC on conversion of monomer.

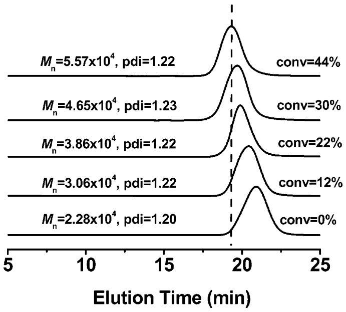


Figure 4. Corresponding SEC curves of the data in Figure 3 at different conversions up to 45%.

To investigate the effect of molecular weight on the liquid crystallinity and elasticity, we prepared a series of PMPCS-b-PnBA-b-PMPCS in small quantity with three different macroinitiators A, B, and C. The data are listed in Table 2. Importantly, they have high M_ns and narrow MWDs ($M_w/M_n < 1.2$), which are prerequisites for a perfect polymer network. Typical SEC profiles of macroinitiator C and its triblock copolymer are compared in Figure 5. It is clear that the macroinitiator peak is shifted to the direction of higher molecular weight, and no shoulders exist after polymerization. Its chemical structure was confirmed by ^{1}H NMR and ^{13}C NMR spectra presented in Figures 6 and 7 separately. The ^{1}H NMR spectrum was also employed to estimate the composition of the triblock copolymers (see Table 2). Calculations were based on the relative intensity of

Table 2. Molecular Weights, MWDs, and Composition Data of the ABA Type Triblock Copolymers Prepared from Different PnBA Macroinitiators

sample	M_n(SEC)[a]	M_w/M_n	M_n(calcd)[b]	wt % (PMPCS)	mol % (PMPCS)[c]	liquid crystallinity[d]
triA-1	54K	1.10	13K−46K−13K	36.11	15.25	no
triA-2	58K	1.15	15K−46K−15K	39.47	16.67	no
triA-3	56K	1.15	18K−46K−18K	43.90	20.00	no
triA-4	67K	1.17	29K−46K−29K	55.77	28.57	yes
triB-1	85K	1.10	9K−84K−9K	17.65	6.54	no
triB-2	88K	1.10	11K−84K−11K	20.75	7.40	no
triB-3	95K	1.15	23K−84K−23K	35.38	14.53	yes
triC	94K	1.13	21K−67K−21K	38.53	16.67	yes
triD	100K	1.12	28K−93K−28K	37.58	15.90	yes

[a] Calibrated by PS standards. [b] Calculated according to the equation $M_n(\mathrm{calcd}) = M_{n,\mathrm{P}n\mathrm{BA}}(\mathrm{calcd}) \times [1 + (1/128.17) \times (m_{\mathrm{MPCS}}/m_{n-\mathrm{BA}}) \times 404]$ ($m_{\mathrm{MPCS}}/m_{n-\mathrm{BA}}$: molar ratio measured by ^{1}H NMR). [c] Molar fraction of PMPCS block was measured by ^{1}H NMR. [d] Examined by POM.

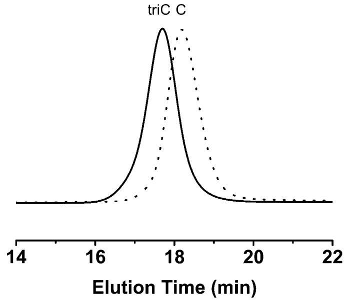


Figure 5. Typical SEC curves of macroinitiator C and its triblock copolymer. Conditions: $T = 110$ °C; solvent: chlorobenzene; $[\mathrm{MPCS}]_0 = 0.25$ M; $[\mathrm{macroinitiator}]_0 = 2.24$ mM; [CuCl]/[PMDETA] = 1.

the methoxy protons of MPCS units (3.0−3.8 ppm, 6H, *k* in Figure 6) and the methyne protons of *n*-BA units (2.1−2.5 ppm, 1H, *d* in Figure 6). The difference between experimental M_n acquired by SEC and that calculated from the ^{1}H NMR spectrum was due to the dissimilar hydrodynamic volumes of coillike PS standards and the triblock copolymer having a rod−coil−rod conformation.

Thermal and Liquid Crystalline Behaviors. Thermal behaviors of PMPCS-*b*-P*n*BA-*b*-PMPCS were examined by DSC. Two distinct glass transitions were clearly detected by DSC for all samples, which indicates the immiscibility of the corresponding blocks. Representative thermograms of triblock copolymers are shown in Figure 8. The signal around −45 °C is identified as T_g of the P*n*BA block and the other around 118 °C as T_g of the PMPCS block. No nematic to isotropic transitions of the samples were observed even when the temperature was raised to beyond 350 °C. T_gs and the temperatures of degradation (T_ds) of representative samples are given in Table 3. The two T_gs move toward each other compared with the values of their homopolymers (−56 °C for P*n*BA and 122 °C for PMPCS), which is a characteristic of block copolymers. It is evident that the good thermal stability of the obtained triblock

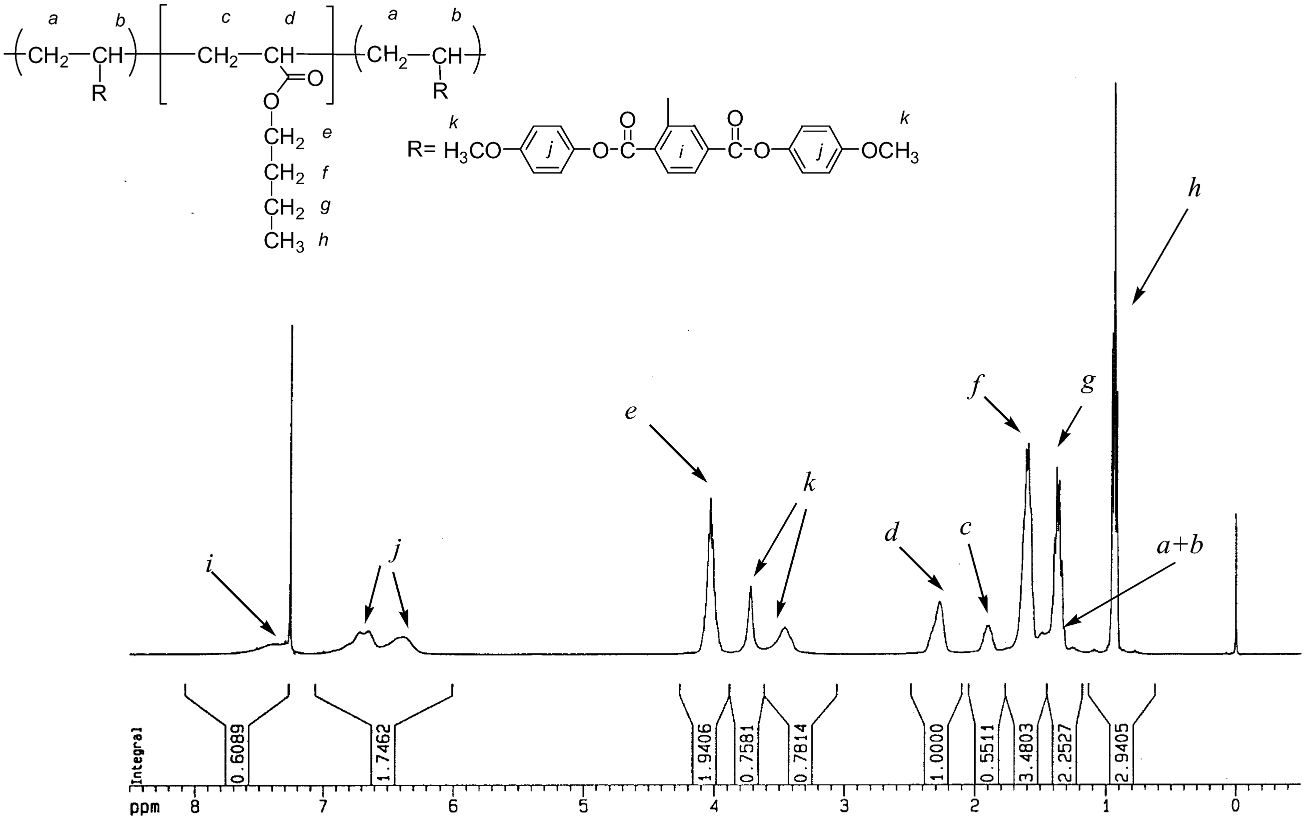


Figure 6. ^{1}H NMR spectrum of PMPCS-*b*-P*n*BA-*b*-PMPCS (sample triC in $CDCl_3$, 400 MHz).

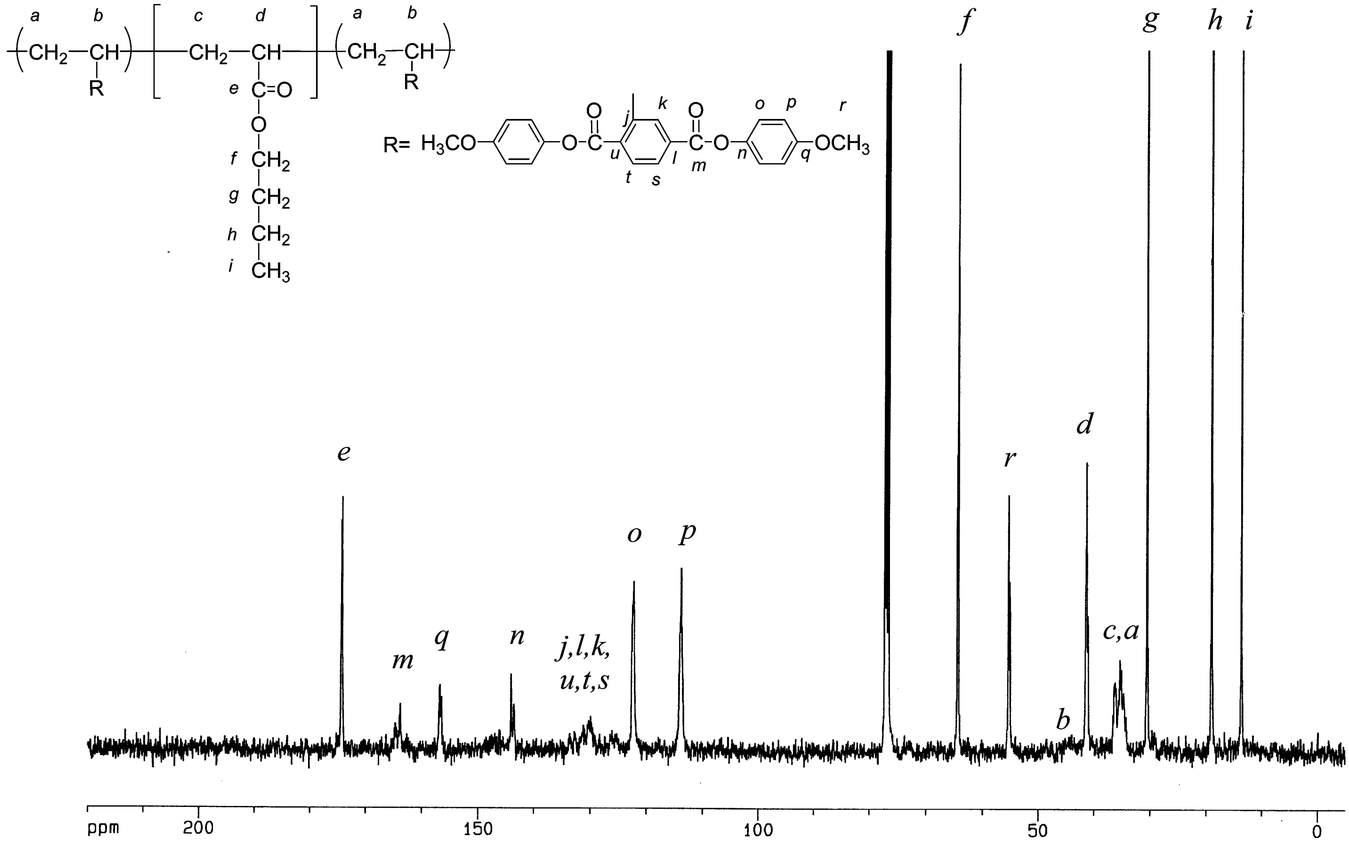


Figure 7. ^{13}C NMR spectrum of PMPCS-*b*-P*n*BA-*b*-PMPCS (sample triC in $CDCl_3$, 400 MHz).

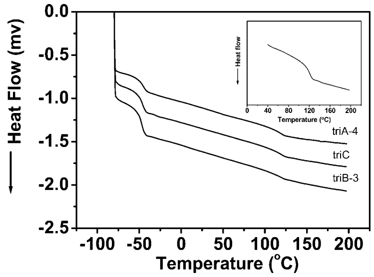


Figure 8. DSC thermograms (−90 to 200 °C) of triblock copolymers on heating at a rate of 10 °C/min under a nitrogen atmosphere. The inset is the DSC trace of a LC PMPCS prepared by ATRP ($M_{n,SEC}$ = 17 500, M_w/M_n = 1.17).

Table 3. Glass Transition and Degradation Temperatures of Some PMPCS-*b*-P*n*BA-*b*-PMPCS and the Homopolymers of PMPCS and P*n*BA[a]

sample	T_g^{PnBA}, °C	T_g^{PMPCS}, °C	T_d, °C[b]
triA-4	−44.82	118.88	383.52
triB-3	−46.28	118.41	375.37
triC	−45.68	117.60	385.87
triD	−45.72	119.60	381.53
P*n*BA[c]	−55.98		286.13
PMPCS[d]		121.49	409.41

[a] Investigated in a temperature range from −90 to 200 °C at a heating rate of 10 °C/min under a continuous nitrogen flow. [b] Temperature at weight loss of 5%. [c] Synthesized by ATRP with $M_{n,SEC}$ = 73 000, M_w/M_n = 1.10. [d] Synthesized by ATRP with $M_{n,SEC}$ = 17 500, M_w/M_n = 1.17.

copolymers results from the incorporation of PMPCS segments.

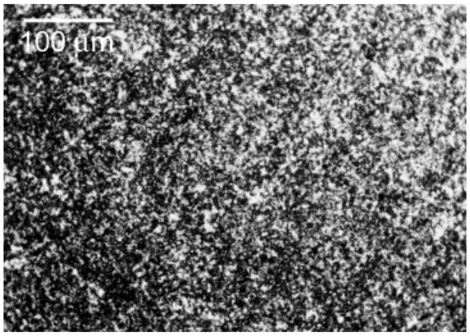


Figure 9. LC texture of sample triC at 150 °C.

Reported studies have demonstrated that the liquid crystallinity of PMPCS depends on its M_n. Only is its M_n calibrated with ^1H NMR beyond 20 000, PMPCS prepared by ATRP develops a nematic phase above its T_g, and no clearing point is detected until decomposition.[23] The rule of the liquid crystallinity dependence of the molecular weight is applicable for PMPCS-containing block copolymers such as PMPCS-*b*-PS and PMPCS-*b*-PMMA. In this situation, no relationship between the LC behavior and the PMPCS segment content of the samples listed in Table 2 was found. Only those with PMPCS block having M_n more than 20 000 are LCPs proved by POM, which is in good agreement with the rule. Figure 9 is the LC texture of the MPCS-containing triblock copolymer.

The mesophase of LC PMPCS-*b*-P*n*BA-*b*-PMPCS was analyzed by WAXD at elevated temperatures. Figure 10 shows the one-dimensional X-ray diffraction pattern of triC in its nematic phase at 150 °C. The intense diffraction peak at $2\theta = 5.9°$ corresponds to an interchain packing distance of 1.5 nm. Considering the fully extended length of the mesogen (1.9 nm), it is clear that the pendant mesogens are tilted around the polymer backbone. The broad halo at $2\theta = 19.0°$ ($d = 0.5$ nm) was ascribed to the average lateral distance between mesogenic units. However, there is a middle peak at

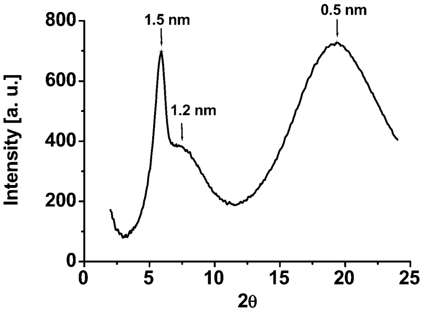


Figure 10. WAXD pattern of sample triC at 150 °C.

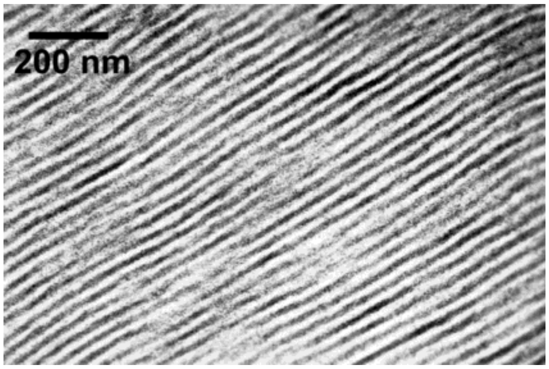


Figure 11. TEM image of triblock copolymer (sample triD). The black areas are PMPCS parts selectively stained by RuO_4.

around $2\theta = 7.2°$ ($d = 1.2$ nm), which is nonexistent in the WAXD curves of homopolymer PMPCS. Therefore, the signal must come from the P*n*BA block. The hypothesis was confirmed by the recent research work of Beiner et al.[25] They found that alkyl side groups of poly(*n*-alkyl acrylates) (P*n*AA) ($n \geq 4$) aggregate in the melt and form alkyl nanodomains with a typical size of 0.5−2 nm. According to their X-ray scattering curve of P*n*BA, a peak centered at $q = 5\ \text{nm}^{-1}$ indicates the exsistence of nanodomains with size of 1.25 nm. Our value is consistent with it.

Among the three LC triblock copolymers, the films of sample triB-3 and triC are elastomeric, while the film of triA-4 is fragile. The reason is that the total M_n of PMPCS blocks must be more than 40 000 to develop a LC phase. Therefore, the middle soft block must have enough high molecular weight to ensure elasticity. On the basis of above studies, we prepared a new elastomeric LC triblock copolymer triD (see Table 2) initiated with macroinitiator D in large quantity. Its morphological and mechanical behaviors were investigated.

Morphological Studies. For most of the all-acrylic TPEs, it is problematic to directly observe the morphologies by TEM due to the low electronic density contrast between the constitutive blocks. Practically, their microphase separation was estimated by tapping mode AFM.[26] However, TEM is effective for the observation of microphase separation of the LC triblock copolymers, as the phenyl groups of the LC blocks can be selectively stained with RuO_4. Because of the high temperature of order−disorder transition (T_{ODT}) (from the results of DMA analysis presented later, T_{ODT} of triD is estimated above 200 °C), we try to get the phase equilibrium of the solution-cast film as closely as possible by controlling the evaporating rate of the solvent.

A typical TEM image is shown in Figure 11. The black parts are ascribed to PMPCS blocks, which locate in the white parts of P*n*BA. In the image, alternating black and white strips are easily discernible. Thus, the microphase separation structure with a long-range order is directly confirmed for the sample.

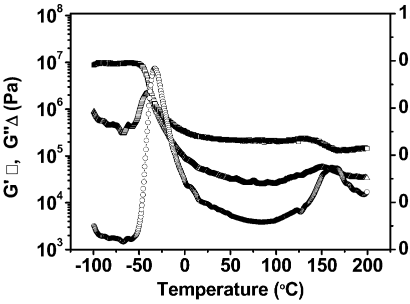


Figure 12. Temperature dependence of shear storage modulus (G'), loss modulus (G''), and the loss factor (tan δ). Heating rate: 3 °C/min; frequency: 1 Hz (sample triD).

In the morphological studies of MJLCP-based triblock copolymer PBBOS-*b*-PS-*b*-PBBOS by TEM, Ober et al.[8d] only found irregular oval nanoaggregates of PBBOS which seem to be breaking up from lamellar regions. Taking account of the similar rodlike mainchains of PBBOS and PMPCS, the difference of the microphase structures may be due to the different properties of PS and P*n*BA.

We must advise that the above morphological results are preliminary and presented just for validating a nanophase-separated system. Comprehensive investigations of the microphase-separated morphological structures of PMPCS-*b*-P*n*BA-*b*-PMPCS are in progress and will be the subject of forthcoming papers.

Dynamic Mechanical Analysis. The dynamic mechanical properties of sample triD were analyzed by DMA in shear mode. It was confirmed that no thermal degradation occurred during the experiment by the identical SEC curves of the sample before and after tests. Figure 12 gives the results of dynamic temperature scan test from −100 to 200 °C at 3 °C/min at 1 Hz. For the curve of temperature dependence of the dynamic shear storage modulus (G'), two transitions are detected and a well-defined rubbery plateau is observed between them. The two features are characteristics of TPEs. No other sharp drop of G' associated with the LC-to-isotropic transition is found within the temperature range, and the sample does not enter into liquid flow region above the T_g of PMPCS block. Both indicate the presence of a very stable nematic phase, and the physical network still persists at least up to 200 °C. Two peaks are found in the curve of loss factor (tan δ) vs temperature, separately related to the glass transitions of the two immiscible blocks. Jerome et al.[18a] reported a broad intermediate transition between the two expected glass transitions in the tan δ curve of PMMA-*b*-P*n*BA-*b*-PMMA obtained by ATRP method. Studies[18a] evidenced that the unexpected transition is detrimental to the mechanical properties, and it is the effect of broad molecular weight distributions of the PMMA outer blocks (consistently with the aforementioned bimodal SEC traces up to 30% conversion during polymerization). In our case, no broad transition is found in the tan δ curve, which means the outer PMPCS blocks are relatively narrowly distributed.

Tensile Testing. A typical stress−strain relationship is presented in Figure 13. The curve shows a large strain corresponding to a low stress. It demonstrates the material is indeed an elastomer. Generally, the ultimate mechanical properties of poly(alkyl acrylates)-containing

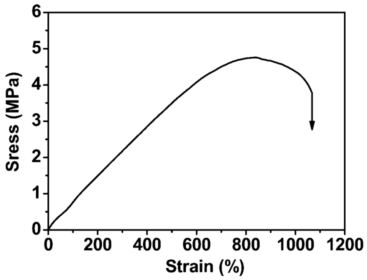


Figure 13. Stress−strain curve for sample triD stretched at the rate of 100 mm/min at room temperature.

TPEs are poor when compared with those of the traditional polydiene-based ones. Jerome et al.[27] calculated the entanglement molecular weight (M_e) for poly(alkyl acrylates) and for polydienes (28 000 for P*n*BA and 1700 for poly(1,4-butadiene)) and ascribed the poor performance to the much larger value of M_e for poly(alkyl acrylates). Although the mechanical properties of PMPCS-*b*-P*n*BA-*b*-PMPCS are not quite good compared to those of SBS due to the reason mentioned above, they are comparable to the reported values of the all-acrylic TPEs.[18b]

We compared the tensile properties of the TLCP prepared by Ikeda et al.[17] with those of the MJLCP-based triblock copolymer. The performance of the MJLCP-based triblock copolymer is superior to those of the TLCP, especially for the elongation at break (only 51% for the TLCP). The main reasons are the relative higher strength of PMPCS domains and the high molecular weight of the MJLCP-based triblock copolymer. Because no data of room temperature stress−strain tests were given in the literature,[15b] mechanical properties of Gronski's and the MJLCP-based triblock copolymer have not been compared. However, it was found that the mechanical properties of Gronski's TPLCP are quite inferior to those of its precursor polymer due to the larger M_e for the middle SCLCP segment.[15b]

Conclusions

A well-defined triblock copolymer based on MJLCP was designed and synthesized by ATRP. The polymerization of the LC monomer, MPCS, was triggered by dibromo-functional P*n*BA macroinitiators in the presence of the CuCl/PMDETA complex. Kinetic study shows that the homogeneous polymerization process is under good control. The SEC traces of block copolymers at different conversions keep monomodal and symmetrical, indicating a high blocking efficiency. The triblock copolymers have high M_ns ($M_n > 70\,000$) and narrow polydispersities ($M_w/M_n < 1.2$). Their chemical structures are proved by NMR. DSC analysis and morphological investigations with TEM of the obtained block copolymers confirm the formation of microphase-separated nanostructures with long-range order. According to the results of POM measurements, the triblock copolymers are LCPs only if the M_n of the outer PMPCS block is beyond 20 000. WAXD spectra of the LC triblock copolymers show a very stable nematic phase in a temperature range from T_g of PMPCS segment to temperature of decomposition. The nanosegregates of the side chain of P*n*BA are also observed.

Among the LC triblock copolymers, sample triB-3, triC, and triD are elastomeric. Preliminary rheological and mechanical tests of triD support the conclusion that the LC block copolymers have the potential as TPEs. DMA data indicate the physical network of the LC block copolymer persists at least up to 200 °C. The mechanical properties of the materials are poor but comparable to the reported results of those of PMMA-*b*-P*n*BA-*b*-PMMA and superior to those of the TLCP prepared by Ikeda et al. Further investigations of the morphological behaviors, the relationship between mechanical properties and morphologies, and the relationship between mechanical properties and liquid crystallinity of the MJLCP-based triblock copolymers are in progress.

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