Notes

Preparation of Discotic Liquid Crystal/Amorphous Block Copolymers and Evidence for Microphase Separated Amorphous/LC Structure

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Introduction

Liquid crystalline (LC)/amorphous block copolymers are interesting macromolecules, because they are anisotropic materials in which organization occurs at different length scales,[1−10] and they form mechanically robust films useful for application purposes. The amorphous block can be used to engineer further the properties of the film. Additionally, there can be interplay between the LC order and domain morphology. For example, Saenger et al.[11] studied polystyrene-*b*-poly[4-(5-(4′-cyano-4-biphenyloxy)pentanoxy)-1-butene]-*b*-polystyrene, an amorphous−nematic LC−amorphous triblock copolymer in which an order−order transition in the copolymer morphology accompanied the nematic LC block's clearing point. The isotropic−nematic phase transition in the LC matrix polymer induced the transition of the polystyrene block morphology from spheres packed in a cubic lattice to hexagonally packed cylinders. It was shown by Anthamatten, et al.[10] and Hajduk, et al.[11] that in amorphous−smectic LC copolymers, microphase separation can interact with the anisotropic structure of the LC smectic block such that the smectic layers within the LC block may be oriented either parallel or perpendicular to the overall lamellar morphology. Schneider, et al.[13] demonstrated that the dimensions of lamellae of poly(hexyl methacrylate)-*b*-poly-[6-(4-(4-(2-butylphenyl)diazo)phenoxy)hexyl methacrylate], an amorphous/chiral LC block copolymer, were influenced by the relative mesogen orientation and also that the loss of the anisotropic structure in the LC phase lead to the formation of a unique gyroid morphology.

Among liquid crystals, discotic LC materials attract particular attention due to their unique properties, such as anisotropic photoconductivity;[14−17] however, there is limited information about synthesis of block copolymers containing main chain or side chain discotic polymer blocks. Knowledge about discotic LC/amorphous block copolymers would be important, because the combination of a discotic phase in a dielectric medium all within one polymeric material should lead to unique photoconductor/dielectric composite materials. Boden, et al.[18,19] reported the synthesis of an amorphous/main chain discotic LC block copolymer and an amorphous/side chain discotic block copolymer. Evidence for microphase separation and discotic LC domain structure for the main chain copolymer was unambiguous. However, evidence for such behavior in the side chain copolymer, poly(*p*-methoxystryene)-*b*-poly(*p*-triphenylene-$(CH_2)_{6\text{ or }10}$-oxystyrene) was obscured by the fact that the clearing temperature of the LC phase was below that of the T_g of the polymer backbone. Because of the dearth of examples of such block copolymers, even less is known about how the discotic structure affects the block copolymer domain morphology.

To study the interrelations of local LC columnar order and overall domain morphology, one must have access to a series of block copolymers in which the lengths and relative volume contents of the discotic and amorphous blocks are varied systematically. Also, for discotic LC blocks with side chain mesogens the polymer backbone should have a low T_g. In this note we present the synthesis of side chain discotic LC/amorphous block copolymers using atom transfer radical polymerization (ATRP) and evidence for their microphase separated amorphous/LC structure. Two monomers, 2,6,7,10,11-pentapentyloxy-3-(3-acryloylpropyloxy)triphenylene (PPAT) and *tert*-butyl acrylate (*t*-BA), were employed as the comonomers, because poly(PPAT) was studied previously and has been shown to possess a discotic columnar structure,[20] and poly(*t*-BA) is an amorphous polymer that can be converted easily into poly(acrylic acid). The resulting block copolymers would then provide us additional access to LC/polyelectrolyte block copolymers.

Experimental Section

Materials. Phenyl 2-bromopropionate was prepared according to the procedure of Haddleton et al.[21] The monomer, 2,6,7,10,11-pentapentyloxy-3-(3-acryloylpropyloxy)triphenylene (PPAT), was synthesized according to the literature.[26] *tert*-Butyl acrylate was distilled from CaH_2 before use. Unless specified otherwise all other reagents were purchased from commercial sources and used as received. All reagents for the polymerizations were handled under nitrogen atmosphere using standard Schlenk techniques.

Measurements. Number-averaged molecular weights (M_n), weight-averaged molecular weights (M_w) and molecular weight distribution (M_w/M_n) were determined using gel-permeation chromatography in THF at 30 °C and a flow rate of 1.00 mL min^{-1}. Three Polymer Standards Services columns (100 Å, 1000 Å, and linear) were connected in series to a Thermoseparation Products P-1000 isocratic pump, autosampler, column oven, and Knauer refractive index detector. Calibration was

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Table 1. Polymerization Data for the ATRP of the Discotic Monomer in Methanol/Benzene Solution

$[M]_o/[I]_o$	solvent (mL)	temp (°C)	time (h)	M_n ($\times10^{-3}$)	DP_n	M_w/M_n	% yield
50	5	65	7	3.2	4	1.0	<5
50	0.5	95	18	6.3	8	1.11	28
50	1	95	3.5	6.6	8	1.02	88
75	1	95	3.5	6.5	8	1.07	83
100	1	95	3.5	5.1	6	1.05	64
50[a]	1	95	4	13.8	17	1.28	59

[a] Chain extension of poly(PPAT) of $DP_n = 8$ (entry 3).

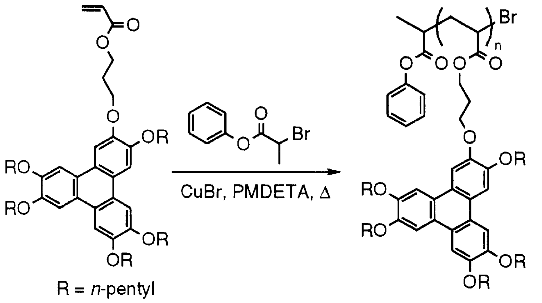
performed using polystyrene samples (Polymer Standard Services; $M_p = 400-1\,000\,000$; $M_w/M_n < 1.10$). ^{1}H NMR spectra (300 MHz) and $^{13}C\{^1H\}$ spectra (75 MHz) were recorded using a Varian Inova Mecury-300 NMR spectrometer. Chemical shifts (δ, ppm) were referenced to the residual proton or carbon signal of the solvent ($CDCl_3$). All polymers were dried overnight under vacuum at room temperature and then at 100 °C for 5 min before their thermotropic behavior was analyzed. The thermal behavior of the monomer and polymers was investigated using a Mettler TA-4000 DSC at a heating/cooling rate of 20° K/min. X-ray diffraction measurements were carried out using a DRON-3.0 diffractometer (Cu Kα radiation, Ni-filtered, transmission mode).

Polymerization of PPAT Using ATRP (Macroinitiator Synthesis). Linear polymers of PPAT were prepared by ATRP in 59 to 88% yield as in the following example (poly(PPAT)-3A from Table 1). Into a dry 25 mL pear-shaped Schlenk flask was added PPAT (1.00 g, 1.27 mmol), Cu^IBr (15.4 mg, 0.110 mmol) and Cu(II)Br_2 (2.6 mg, 9.2×10^{-3} mmol). The flask was evacuated and back-filled with N_2. A degassed mixture of CH_3OH and benzene (1.00 mL total, 4:1 ratio), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) (23.0 μL, 0.110 mmol) and phenyl 2-bromopropanionate (4.0 μL, 2.0×10^{-2} mmol) were added to the flask using syringes that had been purged with N_2. The reaction mixture was heated in a constant temperature oil bath at 95 °C for 3.5 h. Then the reaction mixture was cooled, diluted with THF, and stirred over alumina to remove copper. The alumina was removed by filtration, and the solvents were removed by rotary evaporation until a minimal amount of liquid remained. The polymer was precipitated into cold CH_3OH and dried overnight under vacuum at room temperature. Yield: 0.88 g (88%). $M_n = 6.56 \times 10^3$, and $M_w/M_n = 1.02$.

Synthesis of Poly(PPAT)-*b*-poly(*t*-BA). Block copolymers of PPAT and *t*-BA were prepared in 56 to 78% yield as in the following example. The macroinitiator, poly(PPAT), (0.288 g), Cu^IBr (3.8 mg) and $Cu^{II}Br_2$ (0.3 mg) were placed into a 25 mL pear shaped Schlenk flask. The flask was evacuated and back-filled with N_2. The following liquid reagents, toluene (0.500 mL), PMDETA (8.0 μL), and *t*-BA (0.237 g), were degassed and added to the flask. The reaction mixture was stirred and heated in a constant temperature oil bath at 75 °C for 8 h. The reaction was cooled, diluted with THF, and stirred over alumina to remove the copper. The alumina was removed by filtration, and solvents were removed by rotary evaporation until a minimal amount of liquid remained. The polymer was precipitated into cold CH_3CH_2OH and dried overnight under vacuum at room temperature. Yield: 0.34 g (59%). $M_n = 9.99 \times 10^3$, $M_w/M_n = 1.12$, $\gamma_{p(PPAT)} = 65.6\%$, and $\gamma_{p(t-BA)} = 34.4\%$.

Results and Discussion

As reported previously by the Russian group,[20,22] the conventional radical polymerization of PPAT using AIBN initiator in benzene at 60 °C does not produce any polymeric product. However, the polymerization of PPAT in bulk (both in the LC phase or in the isotropic melt), methanol, or benzene/methanol solutions yielded oligomeric material with a maximum molecular weight (M_n) of 6.5×10^3. Similar observations were made for the free-radical polymerization of two other triphenylene acrylates.[23] We examined the polymerization of PPAT using ATRP (eq 1), and the results are summarized in Table 1. Polymerizations conducted in toluene at low or high concentrations yielded little or no polymer, though in 4-to-1 methanol/benzene mixtures the polymerization yield increased to around 80%. The molecular weight (M_n) of polymer did not vary significantly as a function of the initial monomer-to-initiator ratio ($[M]_o/[I]_0$), and in each case the average degree of polymerization (DP_n) did not exceed eight units. This polymerization behavior contrasts to the ATRP behavior of most acrylates, even though the molecular weight distributions were monomodal and narrow ($M_w/M_n = 1.02-1.11$) in every case. With the exception of the molecular weight distributions, the data were similar to what was observed previously for the conventional radical polymerization of PPAT and were consistent with the proposed mechanism of polymerization of this monomer.[20,22] Talroze et al. proposed that the disklike PPAT most likely forms aggregates of approximately eight molecules in both solution and melt. Chain propagation proceeds within these aggregates in which the steric conditions are sufficiently good for contact of the acrylate units, but steric interactions between aggregates prevent chain propagation from one aggregate to another.



(1)

Even though we do not observe molecular weight control in the ATRP of PPAT, the resulting oligomers appear to be effective macroinitiators for further polymerization. For example, if an oligomer of $DP_n = 8$ is added to more PPAT and ATRP catalyst and heated, then we obtained a polymer in greater than 50% yield with $DP_n = 17$ and a narrow molecular weight distribution ($M_w/M_n = 1.28$) (Table 1, last entry). Thus, it appeared that the macroinitiator underwent a chain extension by the length of another eight-unit aggregate. One might expect that repetition of this process should provide longer chains of poly(PPAT). More detailed work is underway to understand these interesting results and the ATRP mechanism of PPAT.

The PPAT oligomers also may be chain extended using *t*-BA (Table 2 and eq 2), yielding copolymers with poly(*t*-BA) blocks of lengths ranging from $DP_n = 6$ to $DP_n = 101$ and molecular weight distributions (M_w/M_n) of 1.08−1.29. The experimental and predicted lengths of the poly(*t*-BA) blocks agreed within the error of the experiment and the GPC measurement (note that the GPC was calibrated using polystyrene standards, so we do not know to what extent the experimental numbers disagree with the absolute molecular weights), except when very high monomer-to-initiator ratios were used (Table 2, last entry). The latter result might simply be due to the challenges of conducting polymerizations with

Table 2. Data for the Block Copolymerization of *t*-BA at 75 °C in Toluene Solution Using the Discotic Macroinitiator ($DP_n = 8$)

$[M]_o/[I]_o$	% yield	M_n ($\times 10^{-3}$)	M_w/M_n	M_n *t*-BA block ($\times 10^{-3}$)	DP_n *t*-BA block	expected DP_n *t*-BA block	*f*, disc. block (vol %)	*f*, *t*-BA block (vol %)
10[a]	78	7.41	1.08	0.85	6	8	89	12
50[a]	59	9.99	1.12	3.4	30	30	66	34
100[b]	62	13.9	1.29	7.7	60	62	47	53
150[b]	56	14.1	1.17	9.5	74	84	32	68
300[c]	69	17.5	1.08	12.9	101	207	26	74

[a] Reaction time = 8 h. [b] Reaction time = 15 h. [c] Reaction time = 24 h.

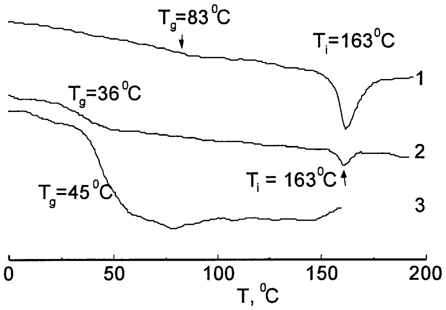
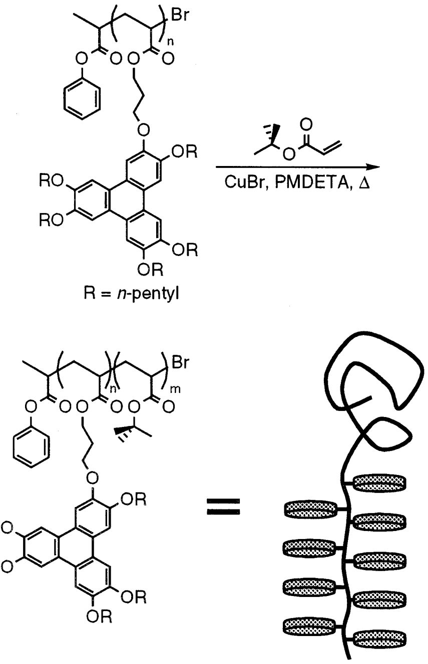


Figure 1. DSC curves for poly(PPPAT), curve 1, the sample corresponding to Table 2, entry 2, curve 2, and poly(*t*-BA), curve 3.

a small amount of initiator and catalyst, as we have not optimized the reaction conditions at this point.



(2)

We then wished to determine whether the copolymer compositions were sufficient to observe microphase separation and formation of the discotic LC phase. Figure 1 shows the DSC curves for the individual components of the block copolymer and the sample corresponding to Table 2, entry 2. Poly(*t*-BA) is an amorphous polymer with T_g at about 40−45 °C, and the thermal behavior poly(PPAT) showed a transition around 163 °C with ΔH = 7.8 J/g that corresponded to the discotic-isotropic phase transition.[20] The presence of both features in the DSC curve of the block copolymer (at 43 and 163 °C) served as evidence for the microphase separated morphology of the material. It is important to note that a decrease in the volume fraction of the discotic block strongly affected the appearance of its feature in the DSC curve of the block copolymer. In the DSC curves of the copolymers with compositions containing a smaller relative amount of the discotic block, this feature was quite small and barely visible.

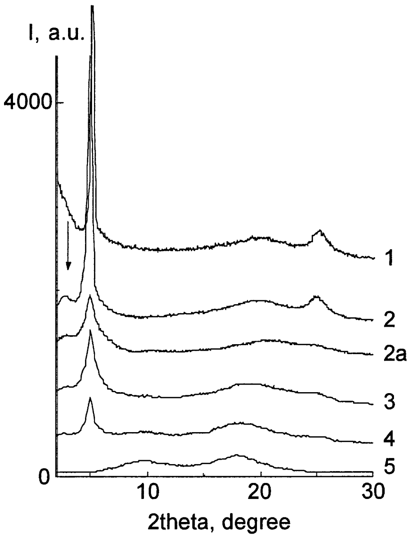


Figure 2. X-ray diffraction patterns for the individual components of the block copolymer (pattern 1 = poly(PPAT) and pattern 5 = poly(*t*-BA)) and the block copolymers of different compositions (pattern 2a = 89 vol % poly(PPAT)—nonannealed, pattern 2 = 89 vol % poly(PPAT), pattern 3 = 66 vol %, and pattern 4 = 47 vol %).

Figure 2 shows the X-ray diffraction patterns for the individual components and block copolymers of different compositions. The two amorphous halos at $2\theta = 9.7°$ and 18° corresponded to the reflections characteristic of poly(*t*-BA). The diffraction pattern for poly(PPAT) with a columnar discotic structure shows both small and wide angle reflections. The wide angle peak (2θ = 25°) corresponded to the 002 reflection with a spacing of d_2 = 0.356 nm and was consistent with a stacking of the side chain disks into columns. In this case the 001 reflection is usually suppressed. The main peak for hexagonal discotics, the 110 reflection,[24] at small angles (2θ = 5.0°) was used to calculate the intercolumnar distance according to usual hexagonal relationship between interatomic spacing and *d* spacing. The spacing, d_1, of 1.75 nm indicated that the columns were packed into a hexagonal arrangement with this average spacing between the centers of the columns. The other peaks were suppressed due to the form factor for such lattices, with a close to sinusoidal distribution of electron density due to the presence of the polymer backbones and to a slight disorder of the columnar structure in polymers.[25]

Annealing the samples above the T_g of both blocks but in the LC phase of the poly(PPAT) block made the signals for the ordered structure more visible in the X-ray diffraction patterns. For example, compare the intensities of the peaks corresponding to poly(PPAT) in Figure 2, patterns 2 and 2a. An additional small angle peak at $2q = 2.75°$ ($d = 3.2$ nm) appeared in the X-ray diffraction pattern (pattern 2) not observed in the patterns for the homopolymers. The appearance of the signal may result from the morphology of the microphase-separated structure, a subject of current investigations.

In summary, PPAT can be polymerized using ATRP, and these polymerizations displayed similar limiting molecular weight behavior as observed in the free-radical polymerization of PPAT. The ATRP of PPAT did not show the same molecular weight control as observed in other acrylate monomers; however, the resulting oligomers had narrow molecular weight distributions and could be used as macroinitiators for further polymerization. Block copolymers of PPAT and *t*-BA were prepared using ATRP chain extension from oligomeric PPAT. The DSC of the block copolymers exhibited thermal transitions consistent with separate phases of poly(*t*-BA) and poly(PPAT), and X-ray scattering of the block copolymers indicated that the poly(PPAT) phase existed as a hexagonal columnar discotic mesophase. We are currently studying the microphase separation morphology of these block copolymers further using electron microscopy and intend to understand how the structure of the discotic LC phase interplays with the block copolymer microphase separation morphologies.

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