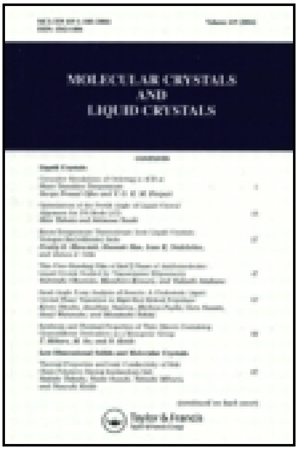

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Anionic Living Polymerization of Monomers with Photo-Electronic Properties for Control of Polymeric Nano Architectures

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Block copolymers, 9-ethylcarbazolyl methacrylate (CzMA) with 3-nitro-9-ethylcarbazolyl methacrylate (NCzMA), and styrene with optically functionalized isocyanates containing disperse red 1 (DR1NCO) and (s)-(-)-2-methylbutanol (MBI), were prepared by anionic polymerization for photo-electronic materials. The living condition of CzMA was found at −78 °C for 3 h with diethyl zinc and block copolymers of CzMA with NCzMA were synthesized successfully. The polymers show potential to be used as energy transfer materials in UV and PL spectra. Block copolymers of styrene with optically functionalized isocyanates were also synthesized with high yield and the polymers showed the large optical activity at 476 nm.

Keywords: anionic living polymerization; block copolymer; photo-electronic properties; nano architecture

INTRODUCTION

The morphology of blended polymer composites has been studied to improve photo-electronic properties [1-2]. The control of morphology by the blending method is difficult because of heterogeneous phase separation between each block. Anionic living polymerization will be the best method to prepare not only controlled polymeric structures but also controlled sized block copolymers [3]. The morphology of the block copolymers obtained by anionic living polymerization can be well controlled because of its covalent bond between A and B blocks.

Since methyl methacrylate containing carbazole moieties have good photoconductivity and nonlinear optical properties, the polymers can be utilized as the luminescence, photorefractive and nonlinear optical materials [4]. Polyisocyanate with chiral center has been studied due to its induced optical activities by the principle of sergeant and soldiers [5] and can be used in many applications such as chiral recognition materials [6], optical switch [7]. It is also expected that copolymer of chiral isocyanate and nonlinear optically functional isocyanate can show various optical effects and be used in many applications.

In this paper, the block copolymers containing photo-electronic properties were synthesized and the optical properties of copolymers were investigated using UV, PL and ORD spectra.

EXPERIMENTAL

9-Ethylcarbazolyl methacrylate (CzMA): Sodium hydride (17.25 g) was slowly added in carbazole (100 g) dissolved in dimethyl formamide (DMF, 1000 ml) at room temperature. After addition of NaH, ethylene carbonate was added to the reaction mixture. The reaction mixture was mechanically stirred at 60 ℃ for 12 h and poured into NaOH solution to filter out the precipitates. The filtered solid was column separated using diethyl ether and hexane with the volume ratio of 3:7.

3-Nitro-9-ethyl-carbazolyl methacrylate (NCzMA): 9-Hydroxyethyl carbazole and 3-nitro-9-hydroxyethyl carbazole, respectively, were reacted with methacrylic acid in THF by using dimethyl carbodiimide (DCC) and dimethyl amino pyridine (DMAP) as the catalysts under ice bath for 5 h. The resulting mixture was column separated using diethyl ether and hexane with the volume ratio of 5:5.

2-[4-(4-Nitrophenylazo)-N-ethylphenyl amino]ethoxy carbonyl amino hexyl isocyanate (DR1NCO): 1,6-Diisocyanatohexane (7.8 ml) was introduced to a reactor at 25 °C. And then, solution of Disperse Red 1 (DR1, 1.7 g) in THF (60 ml) was added dropwise with vigorous stirring. The reaction mixture was vigorously stirred for another 12 h. Large amount of dry n-heaxane was added into the mixture to get precipitation under nitrogen atmosphere, and the precipitate was obtained by filtering the solution and washed by dry n-hexane.

(s)-(-)-2-Methyl-1-butyloxy carbonyl amino hexyl isocyanate (MBI): This monomer was prepared from the reaction of 1,6-diisocyanatohexane and (s)-(-)-2-methylbutanol by the similar procedures as above.

All the polymerizations were carried out under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals. Polymer was obtained as precipitates by pouring reaction solution into a large excess of methanol. The resulting polymers were freeze dried from the benzene solution *in vacuo* overnight.

RESULTS AND DISCUSSION

In the polymerization of CzMA with diethyl zinc, the living character with 100% yield of polymer was obtained at the reaction time of 3 h.

TABLE 1 Poly(CzMA)s and poly(CzMA-b-NCzMA)s with K-Naph. and Zn(Et)$_2$ at –78°C

CzMA/NCzMA	Initiator, mmol			M.W.	M.W. [a]	Time	Yield	Mw/Mn
mmol	K-Naph	DPE	Zn(Et)$_2$	calc.	obsd.	min.	%	
1.00 / -	0.06	0.17	0.64	9,300	9,700	30	34	1.25
3.92 / -	0.08	0.15	1.00	27,300	40,000	180	100	1.48
1.733 / 0.317	0.10	0.12	0.341	10,000/2,000	17,000	180	100	1.32
2.102 / 0.483	0.089	0.130	0.182	13,000/3,500	17,000	180	100	1.34

[a] Determined by SEC using polystyrene standard in THF.

The living polymer showed narrow molecular weight distribution (MWD). Block copolymer of CzMA with NCzMA was synthesized using the living condition of CzMA and it also showed narrow MWD and controlled molecular weight. (Table 1)

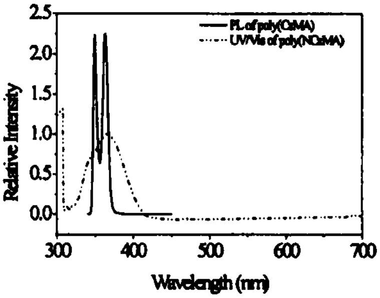

FIGURE 1 PL and UV/Vis spectra of CzMA and NCzMA, respectively.

Figure 1 shows the PL spectrum (solid line, Acton Research Co. SP-300i) of the poly(CzMA) and the UV/Vis (dotted line) spectrum of the poly (NCzMA). The emission and absorption maxima of the poly (CzMA) and poly (NCzMA) were 349 and 368nm, respectively. The spectral overlap indicates that the energy transfer can take place efficiently from CzMA to NCzMA in block copolymer.

TABLE 2 Poly(DR1NCO)s by anionic polymerization at –98 °C in THF

NaNaph[a] mmol	Oct-NCO[b] mmol	15C5 mmol	DR1NCO mmol	Time min.	M. W. calc.	M. W.[c] obsd.	MwMn	Yield %
0.092	0.216	0.950	1.24	30	8,600	11,600	1.07	62
0.087	0.525	0.853	0.99	80	12,800	11,600	1.25	84
0.139	0.141	1.140	1.48	120	9,800	12,800	1.28	94

[a] Sodium naphthalenide as an initiator. [b] Octyl isocyanate as an additive. [c] Determined by SEC using polystyrene standard in THF.

Table 2 shows the polymerization results of DR1NCO in THF at –98 °C. The yield of polymer increases with reaction time and optimum reaction time to obtain the polymer with very high yield was the 120 min at –98 °C. Molecular weight distributions of the polymers are narrow, and the calculated molecular weights of polymers coincide with the real values.

TABLE 3 Poly(St-b-(MBI-r-DR1NCO))s at –78 °C and –98 °C

Na-Naph mmol	Oct-NCO mmol	15C5 mmol	St mmol	MBI mmol	DR1NCO mmol	M. W. calc.	M. W.[a] obsd.	M_w/M_n	Time min.	Yield %
0.083	0.600	0.794	3.37	0.460	0.240	14,600	24,000	1.89	10/60	94
0.146	-	1.56	22.7	2.50	0.550	43,500	35,000	1.78	10/240	82

[a] Determined by SEC using polystyrene standard in THF.

To induce optical activity, random copolymers between DR1NCO and MBI were also synthesized. Optical rotation of the polymers show a tendency to increase with increasing chiral contents and each polymer shows higher value than corresponding chiral monomer (MBI, $[\alpha]_D^{25}$ = -5.4) with an opposite sign. Polyisocyanate usually shows both light scattering phenomena due to liquid crystalline property and low thermal stability with low glass transition temperature. To increase the glass transition temperature, a block copolymer with styrene was synthesized and two functional isocyanates were randomly introduced to living polystyryl anion. Table 3 shows the results of the block copolymerization. Total yield of the polymer was 80–90 % and it depends on the feed ratio of the monomers.

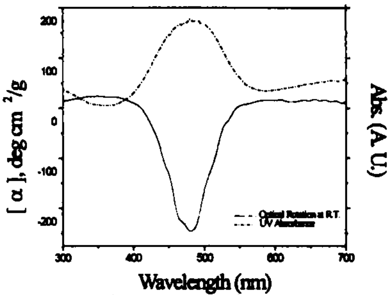

FIGURE 2 ORD and UV spectr of Poly(St-b-(MBI-r-DR1NCO))s.

T_g of the block copolymer was 104 °C, and transparent film was obtained. In the block copolymer, each functional isocyanate block is designed to spheres with 6–10 nm dispersed in styrene matrix. The polymers show high optical activity at 476 nm which corresponds to the absorption maximum of DR1NCO as shown in Figure 2. This can be interpreted by Cotton effect. It is expected, therefore, that these materials have potential to be used as chiral waveguide materials or photonic crystals by controlling the size of styrene or isocyanate blocks.

CONCLUSIONS

Living condition of CzMA with carbazole moiety was confirmed via anionic polymerization. Block copolymers of CzMA with NCzMA have been successfully synthesized by using the living character. The polymer shows the possibility of efficient energy transfer between two blocks in UV and PL spectra. Block copolymers of styrene with optically functionalized isocyanates have also been synthesized with high yield. The polymers show the maximum optical rotation at 476nm. The optical activity seems to be originated from the DR1NCO induced by the chirality of MBI. By controlling the contents of each block in the block copolymer, we expect that nanostructures with very narrow size distribution and controlled electrical and optical properties with the anionic synthetic method reported here.

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