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Anionic polymerization of 4-(9-carbazolyl)methylstyrene

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Abstract

For the application of conjugated polymers in photonics, we synthesized styrene derivatives containing carbazole, 4-(9-carbazolyl)methylstyrene (CMS). The anionic polymerization of CMS was carried out in THF at either −45 or −78°C. It takes around 24 h to get PCMS with 100% yield in THF at −78°C, due to the crystallization of CMS at this temperature. However, the yield exceeded 90% within 10 min. On the other hand, the yield of CMS at −45°C levels up at about 67%, after 30 min. The molecular weight distributions of PCMS obtained at −45°C are broader than those of PCMS synthesized at −78°C. This may be due to the side reactions, such as methylene proton abstraction at the propagating end groups at higher polymerization temperature of −45°C. The glass transition temperature of the polymer measured by DSC was observed in the range of 159–173°C. © 2001 Published by Elsevier Science Ltd.

Keywords: Anionic polymerization; PCMS; Proton abstraction

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1. Introduction

A number of studies have been dedicated to develop anionic living polymerization of styrene derivatives [1]. Nakahama and his co-workers [2–5] have demonstrated in their pioneering works that a wide variety of styrene derivatives with functional groups successfully undergo living anionic polymerization by either protecting functional groups or careful setting polymerization variables such as initiator, temperature and solvents. They have also studied several styrene derivatives having electron-withdrawing groups to develop new living polymer systems under the condition of anionic polymerization [2–5].

Recently, various monomers having electron-withdrawing groups have been studied to develop new living polymer systems. The electron-withdrawing groups play an important role in stabilizing the propagating carbanion thus preventing the side reactions between the carbanion and the electron-withdrawing functional groups. The stabilization of the propagating carbanion was contributed by conjugation of both the electron-withdrawing group and the terminal carbanion [6].

Polymers containing carbazole have interesting properties, such as photorefractivity [7,8], second-order nonlinear optical [9–11] and photoconductive properties [12,13]. However, it is difficult to polymerize *N*-vinylcarbazole by anionic polymerization due to the high electron density of β-carbon associated with N–C=C group [14,15]. The related 2-vinyl-, 3-vinyl- and 4-vinyl-*N*-alkylcarbazole monomers undergo efficient anionic polymerization, producing living type polymers [14,15]. The alkyl group of carbazole, however, disturbs the excimer formation between carbazoles following decrease in the properties of carbazole such as luminescence [15].

In this study, we designed a styrene derivative monomer well known in the anionic polymerization, 4-(9-carbazolyl)-methylstyrene (CMS), having optical properties, such as photorefractivity and electroluminescence, to both synthesize a block copolymer and study luminescent properties in block copolymers without disturbing excimer formation by alkyl group. CMS was polymerized using K-Naph. in THF at either −45 or −78°C to get polymers with controlled molecular weight (MW). We propose the side reaction mechanism during the polymerization of CMS in THF at −45°C.

2. Experimental

2.1. Materials

4-Vinylbenzyl chloride (Aldrich, 90%) was passed through the alumina column and distilled under vacuum (110°C, 3 mmHg) to remove inhibitors. Carbazole (Acros)

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was purified by crystallization from ethyl alcohol (Fisher Scientific) solution before use. Other chemicals were used without further purifications. Free metal naphthalenide, K-Naph., was prepared by the reactions of a small excess of naphthalene with the corresponding alkali metal at room temperature in THF [16,17]. The initiator was stored at −30°C in ampoules equipped with break seals. The concentration of K-Naph. was determined by colorimetric titration to colorless end point with *n*-octyl alcohol in a sealed reactor through break seals under vacuum at room temperature [16,17]. Styrene (Aldrich) was passed through an alumina column, washed with aqueous NaOH solution to remove inhibitors, then rinsed with water, dried for 24 h over $MgSO_4$ and distilled at 25°C under reduced pressure.

2.2. Synthesis of monomer

Carbazole was reacted with 1.5-fold excess of 4-vinylbenzyl chloride in benzene/water using NaOH as a base, and benzyltriethylammonium chloride as phase catalyst to afford CMS at 80°C for 5 h [9,18] (Scheme 1). The reaction mixture was extracted with chloroform and the organic layer washed with water, evaporated and washed with hexane several times. The solid was dissolved in and recrystallized from diethyl ether at −20°C, yield: 80%. The solid monomer was dried over P_2O_5 at 10^{-6} mmHg for 1 week and then dissolved in anhydrous THF and stored at −30°C in glass ampoules under high vacuum.

^{1}H NMR (DMSO-d_6, tetramethylsilane) (ppm): δ 5.73 (1H, $CH_2{=}CH$), 5.18 (1H, $CH_2{=}CH$), 5.65 (2H, CH_2), 6.64 (1H, $CH_2{=}CH$), 7.35, 7.13, 8.18, 7.44, 7.21, 7.61 (12H, Ar–H); ^{13}C NMR (DMSO-d_6, tetramethylsilane) (ppm): δ 45 ($-CH_2-$), 114 ($CH_2{=}$), 136 ($=CH$), 137, 127, 126, 136 (phenyl group), 122, 119, 109, 120, 126, 140 (carbazole); FT-IR (KBr) (cm^{-1}): 3070, 3030 (aromatic C–H), 2950 (aliphatic C–H), 1625, 1595, 1480 (aromatic C=C), 1330 (*tert*-C–N), 1150 (aliphatic C–N); UV/Vis λ_{max}: 343 nm; m.p. 174°C.

2.3. Anionic polymerization

Anionic polymerizations were carried out in THF under high-vacuum conditions (10^{-6} mmHg) for 5 min to 24 h in an all-glass apparatus equipped with break seals in the usual manner [19,20]. For the homopolymerization of CMS, a THF solution of the CMS was added to K-Naph. solution in THF at −45 or −78°C and allowed to react for 5 min to 24 h, and then terminated with methanol. The polymers were precipitated in large amount of methanol, dried, dissolved in benzene and freeze-dried. The yield of polymer was determined from ^{1}H NMR data.

PCMS; ^{1}H NMR (DMSO-d_6, tetramethylsilane) (ppm): δ 0.8–1.2 (2H, CH_2–CH), 1.5–1.8 (1H, CH_2–CH), 4.7–5.0 (2H, $-CH_2$), 5.8–6.5 (4H, phenyl), 7.9–8.2, 7.0–7.4 (8H, carbazole); FT-IR (KBr) (cm^{-1}): 3038 (aromatic C–H), 2910 (aliphatic C–H), 1625, 1595, 1480 (aromatic C=C), 1330 (*tert*-C–N), 1150 (aliphatic C–N); T_d: 416°C; T_g: 173°C.

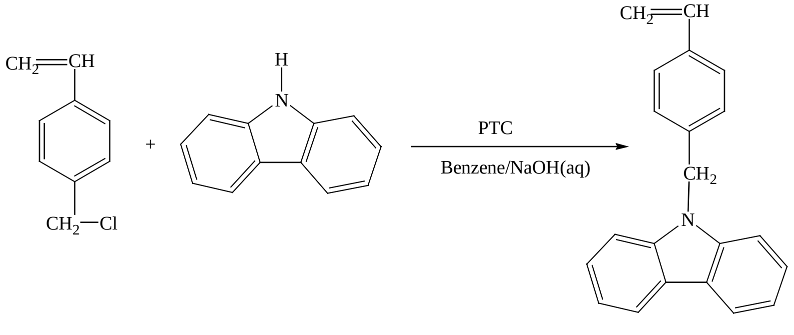
2.4. Block copolymerization of CMS with styrene

Styrene was polymerized with K-Naph. in THF at −78°C in all-glass apparatus in vacuo. After 30 min, a portion of living polystyrene was withdrawn to attached receiver to determine characteristic of the homopolymer. The second monomer, CMS, in THF solution was added to the living homopolystyryl solution in THF solution, polymerized for 24 h at −78°C, terminated with methanol, and precipitated in the large amount of methanol. Also, the reverse triblock copolymer between CMS and styrene, PS-*b*-PCMS-*b*-PS, was synthesized by sequential addition of CMS and styrene.

PCMS-*b*-PS-*b*-PCMS and PS-*b*-PCMS-*b*-PS; ^{1}H NMR (DMSO-d_6, tetramethylsilane) (ppm): δ 0.8–1.2 (2H, CH_2–CH), 1.5–1.8 (1H, CH_2–CH), 7.9–8.2, 7.0–7.4, 5.8–6.5 (aromatic), 4.7–5.0 (2H, $-CH_2$). FT-IR (KBr) (cm^{-1}): 3038 (aromatic C–H), 2910 (aliphatic C–H), 1625, 1595, 1480 (aromatic C=C), 1330 (*tert*-C–N), 1150 (aliphatic C–N).

2.5. Characterization

The polymers were characterized by size exclusion chromatography (SEC, Waters M 77251, M510). MWs of the polymers were estimated by using SEC with four columns (HR 0.5, HR 1, HR 3 and HR 4, Waters Styragel columns run in series. The pore size of the columns is 50, 100, 10^3 and 10^4 Å, respectively) with a refractive index detector at a flow rate of 1 ml/min using THF as elution solvent, at 40°C and calibrated relative to polystyrene standards (American



Scheme 1.

Polymer Standards). The polymer was characterized by ^{1}H FT-NMR (JEOL JNM-LA300WB 300 MHz ^{1}H), and FT-IR (Perkin Elmer System 2000). Thermal properties were characterized by TGA (TA2050) and DSC (TA2010) at heating rate 10°C/min. Ultraviolet spectrum of the polymer was recorded in the range of 200–800 nm with a Shimadzu UV-3100 spectrophotometer. Photoluminescence (Acton Research SP-300i) spectra were measured by using a He–Cd laser operating at 325 nm, which was sufficient to excite electrons above the band gap, and 30 mV of the purse power was used to measure the response.

3. Results and discussion

3.1. Homopolymerization of CMS

CMS is soluble in a wide range of organic solvents such as DMF, DMSO, THF and so on. However, it is insoluble in most nonpolar solvents such as hexane, benzene, etc. The polymerization of CMS was attempted with K-Naph. in THF at either −45 or −78°C (Fig. 1). In each case, the reaction mixture always showed a deep red color during the course of the polymerization. The characteristic red color indicates the formation of styryl anion derived from CMS. The red color remained in THF even after 24 h, however, it immediately disappeared upon addition of a small amount of methanol to quench the polymerization, indicating the existence of the living ends [2–5,21,22].

Table 1 shows the homopolymerization results of CMS in THF at −45°C under high vacuum condition (runs 1–4 in Table 1). The yield of the polymer levels up after 30 min. The MWD of PCMS was broad, about 2.0, and SEC curve of PCMS has shoulder (Fig. 2(a)). Also, the observed MW is higher than the calculated value from [M]/[I] ratios. In the anionic polymerization of (3-vinylphenyl)methyl methyl sulfide, reported by Nakahama et al., gelled polymeric materials were obtained during polymerization in THF at −78°C due to the radical combination, induced by 1,6-elimination at the reactive chain end, to form a crosslinked network [2–5]. Also, Nakahama and co-workers [6] reported the polymerization results of hexynylstyrene derivatives at higher temperature, 20 and 40°C. The SEC curve showed multimodal peaks due to the proton abstraction after the completion of the polymerization. However, there is no crosslink reaction observed during and after polymerization of CMS [2–5]. This means there is no radical forming reaction during polymerization. Therefore, it may be due to the undesirable side reaction such as the methylene proton abstraction by reactive chain end in THF at −45°C (Scheme 2). The propagating chain end derived from PCMS is deactivated at −45°C. Probably, the reason of this deactivation is the proton abstraction from

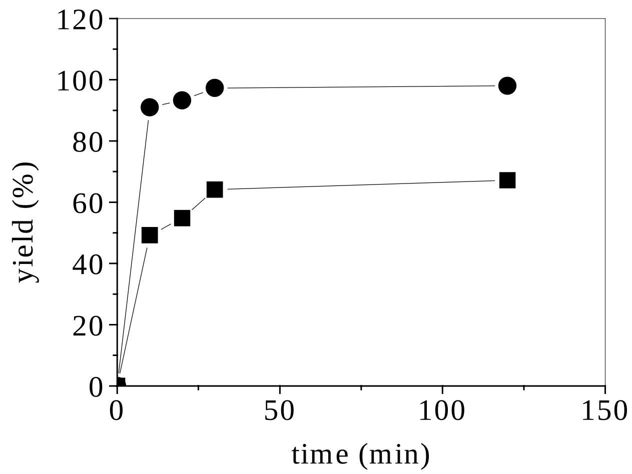


Fig. 1. Time–conversion plots of the CMS polymerization by using K-Naph. as initiator in THF at −45°C (■) and −78°C (●).

Table 1
Anionic polymerization of CMS in THF at −45 and −78°C with K-Naph. as initiator

Run	Amount of reagents (mmol)			Time	Temperature (°C)	Yield[a] (%)	M_n		M_w/M_n[b]
	K-Naph.	Styrene	CMS				Calculated[c]	Observed[b]	
1	0.099		1.715	10 min	−45	49	4800	8500	2.05
2	0.100		1.731	20 min	−45	55	5500	10,000	2.09
3	0.102		1.700	30 min	−45	64	6000	10,500	2.04
4	0.099		1.667	120 min	−45	67	6500	10,000	2.11
5	0.095		1.613	10 min	−78	91	8700	9600	1.67
6	0.097		1.686	20 min	−78	94	9200	9700	1.58
7	0.104		1.819	30 min	−78	97	9500	9500	1.65
8	0.096		1.536	24 h	−78	98	8900	8800	1.55
9[d]	0.091	5.552	2.030	30 min /24 h	−78	99	25,000	30,000	1.48
10[e]	0.104	5.437	0.888	24 h/30 min	−78	99	16,000	18,000	1.35

[a] Measured by NMR.

[b] Measured by SEC using PS standard.

[c] M_w of CMS × 2 × [CMS]/[initiator].

[d] First monomer styrene, second monomer CMS.

[e] First monomer CMS, second monomer styrene.

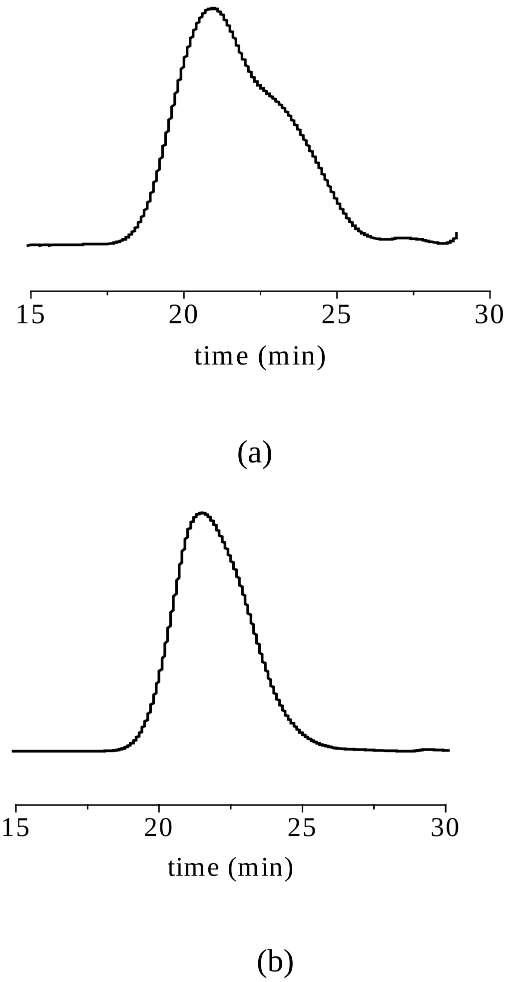


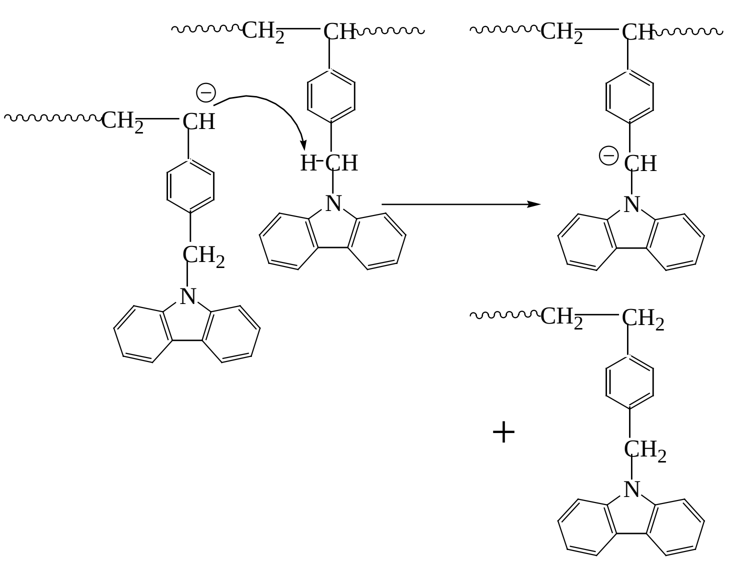
Fig. 2. SEC profile of PCMS synthesized in THF at −45°C (a) and −78°C (b) with K-Naph. as initiator.

the methylene group of the CMS, because the proton is known to be acidic [2–6].

Table 1 also shows the homopolymerization results of CMS in THF at −78°C under high vacuum condition (runs 5–8 in Table 1). The yields of the polymers in THF at −78°C rapidly increased in the initiation step. The yield reached 91.0% within 10 min but slowly increased to 98.0% within 1 day (Fig. 1). It may be due to the crystallization of the monomer at −78°C during the polymerization, and slowly dissolved again in THF. Therefore, it takes long time to get 100% yield. The observed MW of the polymer was in good agreement with the calculated MW. However, the MWD is still broad even when polymerization was carried out at low temperature due to both the crystallization of the monomer leading to inhomogeneous solution during the polymerization and the side reaction. Therefore, it is highly difficult to get narrow MWD even in dilute solution. However, still unimodal peak was observed without shoulder. It appears that any possible side reactions mentioned in previous could be eliminated or reduced at −78°C.

3.2. Block copolymerization

Table 1 also shows the block copolymerization result between styrene and CMS in THF at −78°C (Fig. 3, runs 9 and 10 in Table 1). The MWD of the homopolymer, polystyrene, is narrow around 1.10. However, the block copolymer showed multimodal behavior, MWD 1.48, due to the impurities in CMS monomer. The propagating polystyryl chain ends were terminated by small amount of impurities remaining in CMS, when styrene was first monomer (Fig. 3(a), run 9 in Table 1). The multimodal behavior of SEC curve for the block copolymer was due to the termination of one or both living polystyryl chain end anions by impurities. However, in PS-*b*-PCMS-*b*-PS (Fig. 3(b), run 10



Scheme 2.

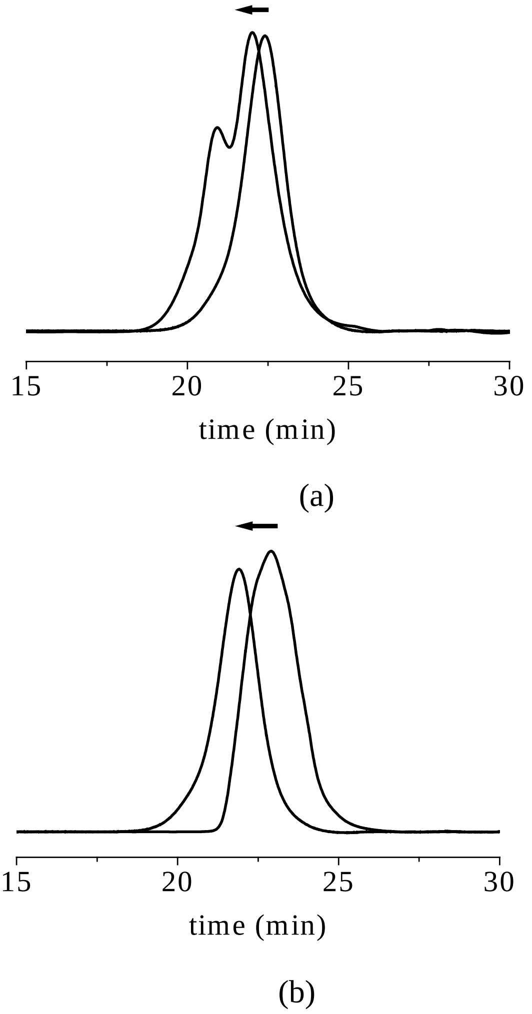


Fig. 3. SEC profile of PCMS-*b*-PS-*b*-PCMS (a) and PS-*b*-PCMS-*b*-PS (b) synthesized in THF −78°C with K-Naph. as initiator.

in Table 1), sharp unimodal peak was observed. The impurities in the CMS solution rapidly reacted with K-Naph. on introducing the initiator solution. Therefore, the PCMS living ends can attack styrene without termination reaction to form block copolymer. Thus, the sequence of monomer insertion to get block copolymer between CMS and styrene is an important aspect of synthesis.

3.3. Thermal analysis of PCMS

The polymer is soluble in a wide range of organic solvents such as THF, DMF, DMSO, benzene and so on. However, it is insoluble in most nonpolar solvents such as hexane. The decomposition temperature (T_d) of the PCMS is 416°C, higher than that of polystyrene, 304°C (Fig. 4) due to the side chain carbazole. The main chain was decomposed at lower temperature, and then carbazole was decomposed at higher temperature. The residue above 450°C could be side chain carbazole. Fig. 4 shows the glass transition temperature (T_g) of the resulting PCMS determined by differential scanning calorimeter (DSC). The T_g value of the polymers ranged from 159 to 173°C for the range of MW 3200–15,100 g/mol (Fig. 5). The T_g values of the polymer increased with the MW of PCMS and became constant at about 170°C. The introduction of carbazole on the phenyl ring increases the T_g value of PCMS more than that of polystyrene, however, decreases the value more than that of poly(*N*-vinylcarbazole) (PVK). The T_g value of PCMS is intermediate between styrene (T_g value of about 100°C) and PVK (T_g value of about 210°C).

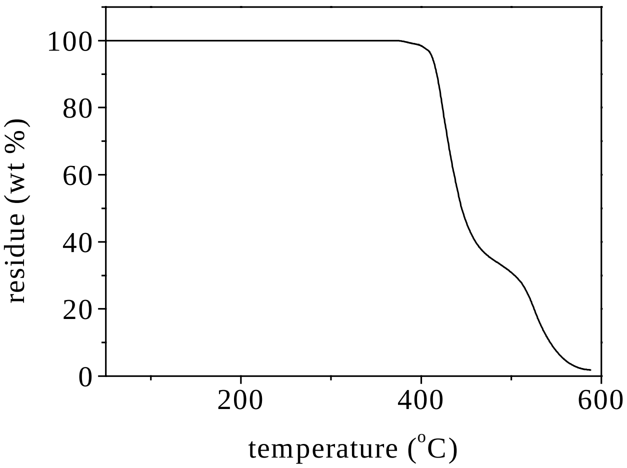


Fig. 4. TGA thermodiagram of PCMS at heating rate 10°C/min in air.

3.4. PL spectrum of PCMS

Fig. 6 shows the photoluminescence (solid line) and the UV/Vis (dotted line) spectra of PCMS, respectively. The emission maximum of PCMS lies at 350 and 365 nm and the absorption maximum lies at 343 nm. At wavelengths below 300 nm, the absorption of benzyl $\pi \rightarrow \pi^*$ transition was observed as an intense signal. Absorptions at 330–350 nm

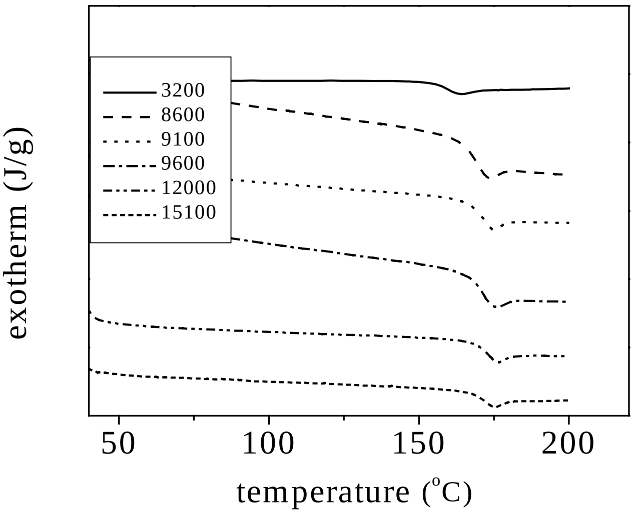


Fig. 5. DSC thermodiagram of PCMSs as a function of MW at heating rate 10°C/min in N_2.

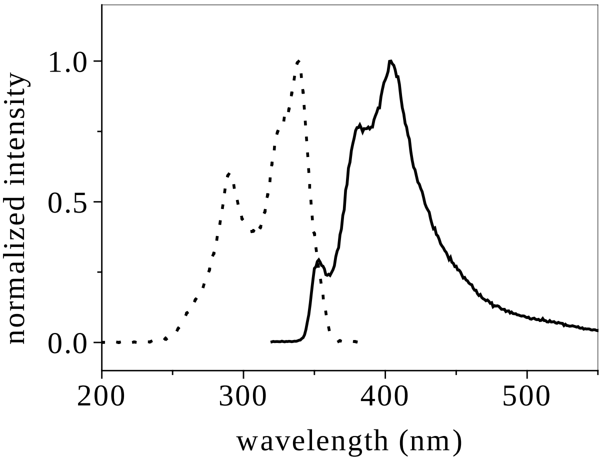


Fig. 6. UV/Vis (dotted line) and photoluminescence (solid line) spectra of PCMS film.

were assigned to the carbazole moiety. The maximum wavelength of photoluminescence of PCMS film was observed in 360.5 and 365.5 nm with a long tail extending to 600 nm probably due to excimer formation of carbazole (Fig. 6).

4. Conclusions

In this study, styrene substituted carbazole, CMS, was synthesized and anionically polymerized. From the SEC results of PCMS at −45°C, the undesirable side reaction, such as the methylene proton abstraction occurred. However, high yield of PCMS with predictable MW and relatively narrow MWD was obtained at −78°C. Also, the block copolymer between CMS and styrene was successfully synthesized in THF at −78°C by sequential monomer addition. Further optical properties of the polymers are under investigation and will be reported.

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