Temperature Dependence of Refractive Index of Films of Well-defined Linear and Star-shaped Polystyrenes

Hiroto Kudo, Hideyuki Aoki, and Tadatomi Nishikubo*
Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221-8686

(Received December 4, 2007; CL-071343; E-mail: nishikubot@kanagawa-u.ac.jp)

Well-defined linear and star-shaped polystyrenes were synthesized, and the temperature dependence of their refractive index (n_D) in the film state was examined. The values of n_D decreased with increasing temperature, with an inflection at the glass-transition temperature (T_g). Above the T_g, the values of difference of n_D between star-shaped polymer and linear polymer increased at elevated temperatures.

Refractive index is a very important physical property for the application of polymers as optoelectronic materials.[1] It is well known that the relationship between the refractive index (n_D), density (ρ g/cm^3), molecular weight (M g mol^{-1}), and molar refraction (R cm^3/mol) of a polymer is described by the Lorentz–Lorenz equation (eq 1).[2]

$$n_D = \sqrt{(M + 2\rho R)/(M - \rho R)} \tag{1}$$

From this equation, it appears that films with a large refractive index should be obtainable from materials with large values of R and ρ. In the previous paper,[3] we reported that star-shaped polysulfides had higher refractive-index values than linear polysulfides. This is because the ρ value of star-shaped polysulfides is higher than that of linear polysulfides. Furthermore, it is expected that the value of n_D of the film will change by heating, because the value of ρ is temperature-dependent. However, no detailed study of the temperature dependence of n_D has been reported. In this paper, we examined the effect of temperature on the refractive index of well-defined linear and star-shaped polystyrenes in the film state. As shown in Figure 1, polymer films prepared by spin-coating on silicon wafers were placed on the heating plate of an ellipsometer, and changes of their refractive index were examined during heating.

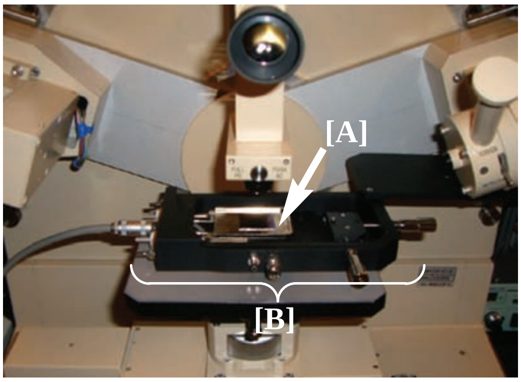
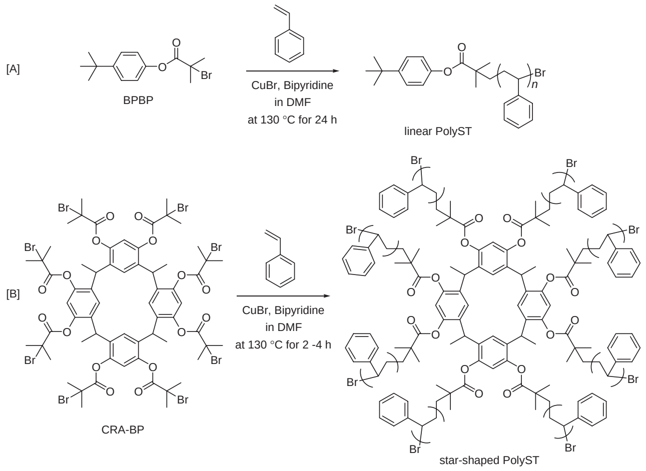


Figure 1. Ellipsometer for the determination of the temperature dependence of refractive index. [A] film of polymer. [B] plate for heating.

Well-defined linear and star-shaped polymers were synthesized by the atom-transfer radical polymerization (ATRP) method (Scheme 1).[4]

The ATRP of styrene was examined using 4-*t*-butylphenyl 2-bromo-2-methylpropionate (BPBP) as an initiator in the presence of CuBr and bipyridine in DMF at 130 °C for 24 h (Scheme 1A). The corresponding linear polystyrenes (polyST) with controlled molecular weight (M_n) and narrow molecular weight distribution (M_w/M_n) were obtained. The structures and M_n's of the obtained polymers were confirmed by ^{1}H NMR spectroscopy and size exclusion chromatography (SEC), respectively.[5] The conditions and results are summarized in Table 1. It was found that the degree of the polymerization (DP) could be controlled by varying the feed ratio of ST (Runs 1–5). Furthermore, ATRP of ST was carried out using a *c*-methylcalix[4]resorcinarene derivative containing eight initiative moieties (CRA-BP) as a core for the synthesis of star-shaped polySTs with a narrow molecular weight range (Scheme 1B). At the feed ratio of ST/CRA-BP = 100/1 for 2 h, the corresponding star-shaped polyST with DP = 22 and M_w/M_n = 1.15 could be obtained in 19% yield (Run 6).[6] Similarly, at feed ratios of ST/CRA-BP = 150/1, 200/1, 250/1, and 300/1 for 2–4 h, the corresponding star-shaped polySTs with DP = 33–61 and M_w/M_n = 1.13–1.17 were obtained in 17–20% yields, respectively (Runs 7–10). That is, well-defined eight-armed star-shaped polymers were synthesized by means of ATRP of ST with low conversion.

A 2-methoxyethyl acetate solution of each polymer was prepared, and this was spin-coated on a silicon wafer, and dried in vacuo at 60 °C for 3 h. The refractive-index values of



Scheme 1. The synthesis of linear and star-shaped styrene polymers.

Table 1. Linear polySTs and eight-armed star-shaped polySTs[a]

Run	Feed ratio	Time /h	Yield[b] /%	M_n[c] (M_w/M_n)	DP[d]	n_D[e]
1	ST/BPBP = 20/1	24	75	2800 (1.18)	20	1.585
2	ST/BPBP = 30/1	24	80	3800 (1.22)	30	1.585
3	ST/BPBP = 40/1	24	85	5400 (1.24)	40	1.585
4	ST/BPBP = 50/1	24	86	6700 (1.19)	50	1.587
5	ST/BPBP = 60/1	24	85	7300 (1.18)	60	1.586
6	ST/CRA-BP = 100/1	2	19	1200 (1.15)	22	1.589
7	ST/CRA-BP = 150/1	2	20	1800 (1.13)	33	1.587
8	ST/CRA-BP = 200/1	2	19	2100 (1.14)	45	1.586
9	ST/CRA-BP = 250/1	2	17	2400 (1.15)	50	1.587
10	ST/CRA-BP = 300/1	4	19	3500 (1.17)	61	1.587

[a] ATRP of ST was carried out in the presence of CuBr and bipyridine in DMF at 130 °C. Linear polySTs (Runs 1–5). Star-shaped polySTs (Runs 6–10). [b] Insoluble part in *n*-hexane. [c] Estimated by SEC (eluent: THF). [d] Calculated by ^{1}H NMR spectroscopy. [e] Measured with an ellipsometer.

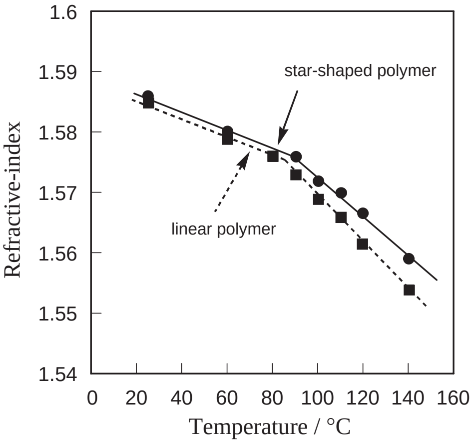


Figure 2. Relationship between refractive-index (n_D) and temperature for linear and star-shaped polySTs.

the resulting films (ca. 0.1-µm thick) were measured by ellipsometry.

The results are summarized in Table 1. The refractive-index values of the linear polySTs and star-shaped polySTs were essentially the same, being in the range of 1.585 to 1.589.

We next examined the effect of temperature on the n_D of linear polyST (DP = 40, Run 4) and star-shaped polyST (DP = 45, Run 8) using an ellipsometer, as shown in Figure 1. The results are shown in Figure 2.

The linear and star-shaped polySTs both showed a linear decrease of n_D as the temperature was increased, with an inflection point at 90–100 °C. The inflection point appeared to coincide with the glass-transition temperature (T_g), which is 92 °C for the linear polyST and 102 °C for the star-shaped polyST. Thus, the values of n_D decreased as a result of the decrease of ρ during heating in the film state. At the transition temperature T_g, the slope of the straight line changed due to the effect of the micro-Brownian motion. The slope of the relationship was larger for linear polyST than for star-shaped polyST, presumably because the segment motion of linear polyST is more active than that of star-shaped polyST, and the decrease of ρ of linear polyST is larger than that of star-shaped polyST. Consequently, the value of n_D of star-shaped polyST is higher than that of linear polyST at temperatures above the T_g.

In summary, we synthesized well-defined linear and eight-armed star-shaped polystyrenes, and examined the temperature dependence of their refractive index values in the film state. The values of refractive index (n_D) decreased with increasing temperature in the film state, and linear relationships between n_D and temperature, with an inflection point at the glass-transition temperature T_g, were observed. At temperatures above T_g, the n_D of star-shaped polyST was higher than that of linear polyST.

This work was supported by a Grant-in-Aid for Scientific Research in Japan (No. 19655084) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 For example: In *Refractive-index Control of Transparent High Polymers*, Gakkaisyuppan Center, Tokyo, **1998**.

2 G. H. Meeten, *Optical Properties of Polymers*, Elsevier Applied Science, London, **1989**.

3 H. Kudo, H. Inoue, T. Nishikubo, T. Anada, *Polym. J.* **2006**, *38*, 289.

4 For example: a) J. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614. b) T. E. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science* **1996**, *272*, 866.

5 Typical spectroscopic properties of linear polySTs. Spectroscopic data of linear polyST obtained by ATRP at the feed ratio of ST/BPBP = 30/1 (Run 2 in Table 1). IR (film, cm^{-1}): 1750 (ν C=O ester), 1600 and 1492 (ν C=C aromatic). ^{1}H NMR (500 MHz, CDCl$_3$, TMS) δ 0.91–1.50 (m, 75H, C(CH$_3$)$_3$, C(O)–C(CH$_3$)$_2$–, and –CH$_2$–), 1.84–2.05 (m, 30H, >CH–), 6.46–7.24 (m, 154H, aromatic H).

6 A typical procedure for the synthesis of star-shaped polySTs was as follows (Run 6 in Table 1): The reaction of CRA-BP (0.022 g, 0.0125 mmol), CuBr (0.015 g, 0.1 mmol), bipyridine (0.032 g, 0.2 mmol), and ST (1.04 g, 10 mmol) was carried out in DMF (1.2 mL) at 130 °C for 2 h in vacuo in a polymerization tube. After that, CHCl$_3$ was added to the resulting mixture and the whole was washed with water several times. The organic layer was evaporated and poured into a large amount of *n*-hexane to precipitate the star-shaped polyST as a white solid. IR (film, cm^{-1}): 1750 (ν C=O ester), 1595 and 1490 (ν C=C aromatic). ^{1}H NMR (500 MHz, CDCl$_3$, TMS) δ 0.50–1.53 (m, 412H, –CH$_3$ of calixarene, C(O)–C(CH$_3$)$_2$–, and –CH$_2$–), 1.86–2.06 (m, 176H, >CH–), 4.50 (broad s, 4.0H, >CH– of calixarene), 6.46–7.24 (m, 888H, aromatic H).

Published on the web (Advance View) February 9, 2008; doi:10.1246/cl.2008.282