Curing Studies of Ladder-Like Poly(allylsilsesquioxane) and its copolymers by Differential Scanning Calorimetry

P. Santhana Gopala Krishnan [*] and **Chaobin He**

Molecular and Performance Materials Cluster, Institute of Materials Research & Engineering
3, Research link, Singapore 117 602
E-mail: sg-krishnan@imre.a-star.edu.sg; psgkrishnan@hotmail.com, Fax: (65) 6872 7528

Summary

Using stepwise coupling polymerization method, three ladder-like poly(allylsilsesquioxane)s have been synthesized. The prepared ladder-like polymers contain (i) allyl, (ii) allyl and methyl and (iii) allyl and phenyl as side chain groups. They were characterized by FTIR, NMR, WAXD, DSC and TGA. Characterization indicated that they had ladder-like structure. All the polymers were cured by 2,2'-dibenzoyl peroxide (1% W/W) and the kinetics for the bulk polymerization of these polysilsesquioxanes was followed by dynamic DSC. The Ozawa and Kissinger methods were used to calculate activation energies for curing of these polysilisesquioxanes. Cured samples were characterized by FTIR, DSC and TGA.

Introduction

Since Brown et al [1] first reported the synthesis of poly (phenylsilsesquioxane) (PPS) in 1960, many were interested in this kind of polymers, since they possess outstanding electrical properties which made them suitable for applications in coatings, electronic and optical devices [2]. Due to the harsh reaction conditions used by Brown to prepare PPS, his method cannot be employed to synthesize reactive ladder-like polysilsesquioxanes (LPS). In late 1980s, a new polymerization method called 'stepwise coupling polymerization' has been reported to synthesize reactive LPS containing hydrogen [3], epoxy [4], maleimide [5], methacrylate [6], amine [7], alcohol [8], liquid crystalline chromophores [9] and non-linear optical chromophores [10] as side chain groups. In this paper, the synthesis of three reactive LPS containing allyl as side chain groups and their curing kinetics by dynamic differential scanning calorimetry (DSC) are reported.

Experimental

Materials

1,4 - phenylene diamine (pPDA), calcium hydride, triethylamine (TEA), dibenzoyl peroxide (BPO), sodium chloride (NaCl), methyltrichlorosilane, phenyltrichlorosilane and allyltrichlorosilane were procured from Aldrich Chemicals. Conc. hydrochloric

acid, toluene, tetrahydrofuran (THF) and anhydrous sodium sulphate (Na_2SO_4) were obtained from Merck. TEA was distilled and pPDA was sublimed before use. Toluene and THF were kept in calcium hydride for few days to remove the moisture present in the solvent and were distilled before use.

Characterization

Perkin Elmer spectrometer 2000 was used to record the FT-IR spectrum of samples. Bruker 400 MHz NMR spectrometer was used for recording NMR spectra at RT using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. DSC 2920 (TA Instruments) was used to study the curing kinetics of LPS. 200 mg of LPS and 2 mg of BPO (1%) were dissolved in 2 mL of THF. Then vacuum was applied to remove THF and the resulting paste was used for curing studies. Molecular weight was determined using a Waters GPC system containing a Waters 2690 separation module and Waters 410 differential refractometer detector. Polystyrene (Polysciences Corporation) was used as a calibration standard and the mobile phase used was $CHCl_3$. Shodex GPC KF-800 column of size 8 mm X 300 mm, flow rate 1 mL/min, injection volume 100 μL and sample concentration 1 mg/mL were used. Weight loss was examined using a Perkin Elmer TGA 7 at a heating rate of 10 °C/min in static air and nitrogen (N_2) atmospheres. Wide angle X-ray diffraction (WAXD) analysis was carried out on a Bruker AXS X-ray diffractomer (GADDS).

Synthesis

Using stepwise coupling polymerization method, three LPS have been synthesized. They are (i) allyl (**HP**), (ii) allyl and methyl (30:70 by mol percent) **(CP-Methyl)** and (iii) allyl and phenyl (30:70 by mol percent) **(CP-Phenyl)** as side chain groups and their chemical structures are given in scheme 1. A typical synthetic procedure used for **CP-Phenyl** is as follows: 5.78 mL (35 mmol) of phenyltrichlorosilane, 2.17 mL (15 mmol) of allyltrichlorosilane, 13.9 mL (100 mmol) of TEA and 75 mL of toluene were taken in a flask fitted with mechanical stirrer. 2.7 g (25 mmol) of pPDA dissolved in 75 mL of THF was added using syringe pump at the rate of 12mL/h. The reaction was carried out overnight under a steady stream of argon gas at -18 °C.
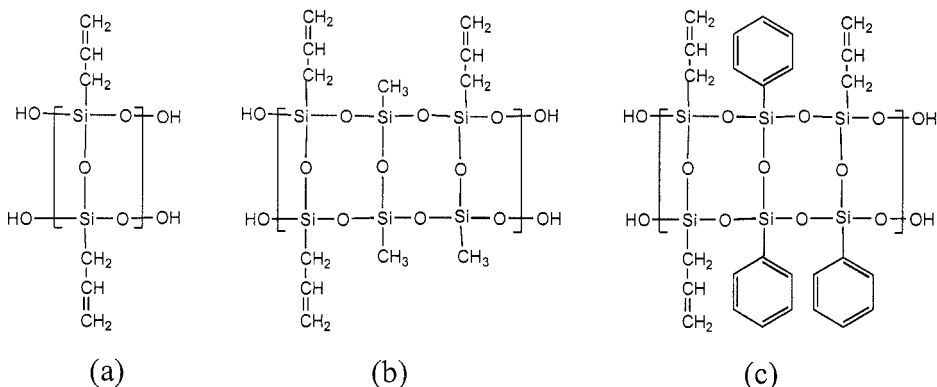
Scheme 1: Chemical structure of LPS (a) **HP** (b) **CP-Methyl** (c) **CP-Phenyl**

Next day, 1.4 mL (77.78 mmol) of deionised water was mixed with 55 mL of THF and were added dropwise using syringe pump at the rate of 10 mL/h to the reaction flask, which was kept at -18 °C and the reaction was carried out overnight. Following day, temperature of the reaction mixture was allowed to gradually rise to RT and held at that temperature for 6 h. Reaction mixture was filtered and the filtrate was washed thoroughly with saturated NaCl solution till the pH was neutral. Then they were dried overnight using Na_2SO_4. To facilitate condensation, 2mL of TEA was added to the filtrate and the solution was stirred at RT for 24 h. Afterwards, the solution was washed with 100 mL of 1.8 % hydrochloric acid solution followed by saturated NaCl solution till the solution becomes neutral. Then the solution was kept in Na_2SO_4 overnight for drying. Solvent was removed to get a viscous liquid. Typical synthetic route is given in scheme 2. Other two LPS were synthesized similar to the above procedure. Based on the assumption that each silicon atom has 1.5 oxygen atoms attached to it, yield was calculated and was found to be 64.5, 53.5 and 58.5 % for **HP**, **CP-Methyl** and **CP-Phenyl** respectively.
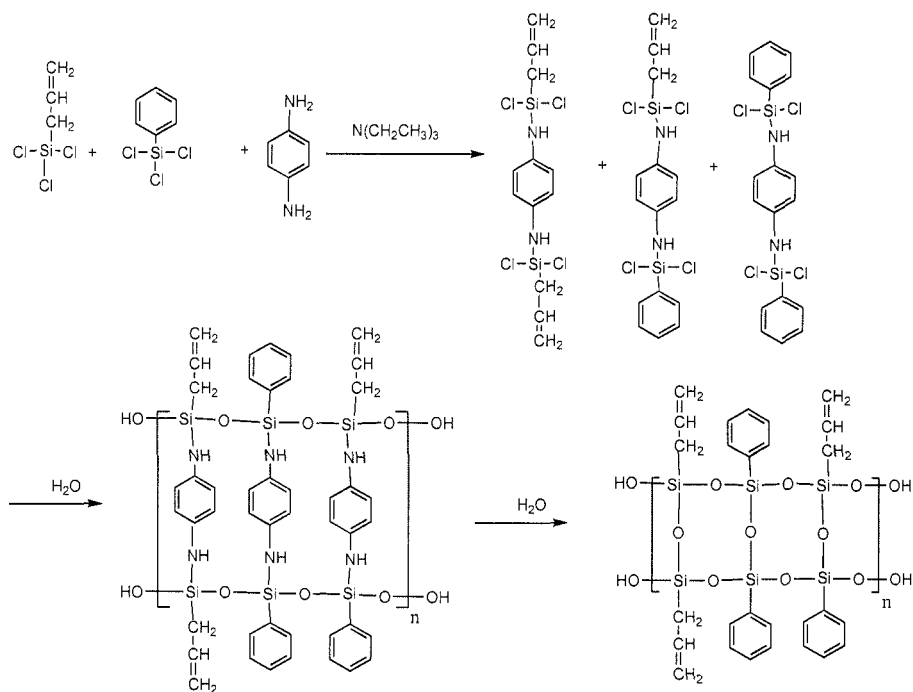
Scheme 2: Preparation of **CP-Phenyl**

Results and Discussion

The possible structures for a polymer derived from a trifunctional monomer are (a) crosslinked polymer (insoluble gel) (b) highly branched polymer and (c) ladder-like polymer with possible defects. In the present study, the first structure is ruled out because **HP**, **CP-Methyl** and **CP-Phenyl** were found to be soluble in common solvents, which suggest that they are not crosslinked. Further, the narrow molecular

weight distributions (PD) (table 1) suggest the existence of well-defined structures and based on this, the highly branched polymer structure was ruled out.

Table 1: Characterization data of LPS

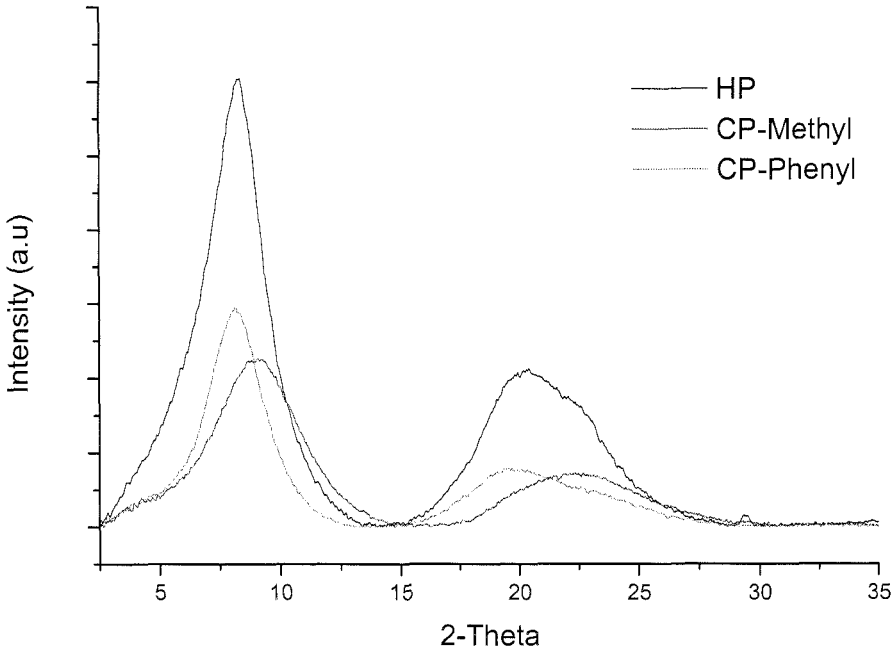| Items	HP	CP-Methyl	CP-Phenyl
IR (cm^{-1})	3410 (ν_{O-H}) 2963 (ν_{C-H}) 1635 ($\nu_{C=C}$) 1418 (δ_{C-H}) 1084 (ν_{Si-O})	3363 (ν_{O-H}) 2962 (ν_{C-H}) 1627 ($\nu_{C=C}$) 1418 (δ_{C-H}) 1089 (ν_{Si-O})	3410 (ν_{O-H}) 2917 (ν_{C-H}) 1630 ($\nu_{C=C}$) 1429 (δ_{C-H}) 1087 (ν_{Si-O})
^{1}H-NMR (δ in ppm)	1.66 (-$\underline{C}H_2CH=CH_2$) 4.99 (-$CH_2CH=\underline{C}H_2$) 5.80 (-$CH_2\underline{C}H=CH_2$)	0.15 (Si $\underline{C}H_3$) 1.66(-$\underline{C}H_2CH=CH_2$) 4.97(-$CH_2CH=\underline{C}H_2$) 5.81(-$CH_2\underline{C}H=CH_2$)	1.58 (-$\underline{C}H_2CH=CH_2$) 4.93 (-$CH_2CH=\underline{C}H_2$) 5.88 (-$CH_2\underline{C}H=CH_2$) 7.17 – 7.75 (Aromatic)
^{13}C-NMR (δ in ppm)	20.5 (-$\underline{C}H_2CH=CH_2$) 115.8(-$CH_2CH=\underline{C}H_2$) 132.6(-$CH_2\underline{C}H=CH_2$)	1.6 (Si $\underline{C}H_3$) 20.2 (-$\underline{C}H_2CH=CH_2$) 115.1(-$CH_2CH=\underline{C}H_2$) 132.5(-$CH_2\underline{C}H=CH_2$)	20.6 (-$\underline{C}H_2CH=CH_2$) 115.8(-$CH_2CH=\underline{C}H_2$) 132.0 (-$CH_2\underline{C}H=CH_2$) 125.7, 128.2, 128.6, 129.5, 130.9, 134.5 (Aromatic)
M_w	6. 4 x 10^3	9.9 x 10^3	7.3 x 10^3
PD	1.06	1.19	1.15
d_1 (A°)	10.7	9.7	10.8
d_2 (A°)	4.4	4.0	4.5

Fig. 1 X - ray diffractogram of LPS

Both ^{29}Si-NMR and XRD studies confirmed the existence of third possibility. Two peaks were observed at about –80 and –70 ppm in ^{29}Si-NMR, which were assigned to SiO$_{3/2}$ and SiO(OH) respectively. XRD of LPSs is given in figure 1. The first halo characterizing the chain-to-chain distance (d_1) in the LPS was narrow and sharp which means that all the three macromolecules had rigid rod-like skeletons in which the movement around the longitudinal axis is limited, and that the conformation and cross-sectional motions were practically invariable. The second diffuse halo covers a wide range of diffraction angles with a peak located at 2θ, giving the thickness of the polymer chains as d_2 and the values are given in table 1 along with IR, NMR and GPC characterization data of the three LPSs.

Kinetics

Dynamic DSC was used to determine the kinetic parameters for the curing kinetics of LPS using Ozawa [11] and Kissinger's [12] equations, which are as follows:

$$\frac{\partial \ln \beta}{\partial \left(\frac{1}{T_p} \right)} = \frac{-1.052\, E_a}{R} \quad \text{(Ozawa)}$$

$$\frac{\beta}{T_p^2} = \left[\frac{AR}{E_a} n \left(1 - \alpha_p \right)^{n-1} \right] e^{-E_a / RT_p} \quad \text{(Kissinger)}$$

where β is the heating rate , T_p is the temperature at the exothermic peak of the DSC curve, A is pre-exponential factor, R is the universal gas constant and E_a is the activation energy for curing.
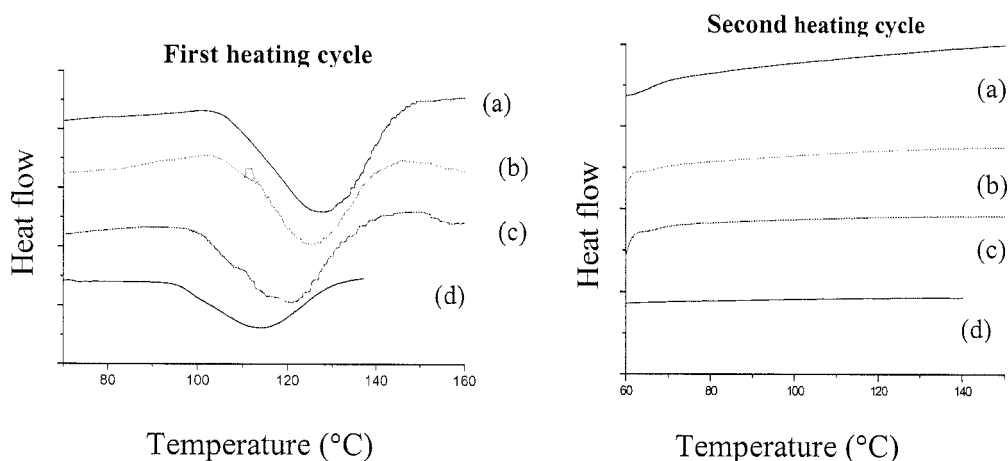

Figure 2: DSC thermograms of CP – Phenyl at
(a) 10 °C/min (b) 7 ° C/min (c) 5 °C/min and (d) 3 °C/min

The assumptions made by Ozawa [11] are that the T_p represents a point of constant conversion for each heating rate and that the temperature dependence of the reaction rate constant obeys the Arrhenius equation. Assuming that the term n(1-αp)n-1 in Kissinger's equation is independent of heating rate, Kissinger [12] proposed that a series of experiments using different heating rates could be used to estimate the E_a from the plot ln of β/T_p2 vs $1/T_p$.

Table 2: Thermal data of LPS

| Items		HP	CP-Methyl	CP-Phenyl
T_p (°C) at different heating rates	3	114.3	114.7	118.2
	5	119.9	118.7	121.0
	7	125.1	123.8	125.3
	10	128.9	127.0	128.7
ΔH (J/g) at different heating rates	3	74.59	33.90	26.33
	5	68.18	38.00	28.10
	7	58.60	30.78	25.87
	10	79.67	40.50	20.98
E_a (kCal/mole)	Ozawa	23.66	27.36	24.76
	Kissinger	23.32	27.22	24.41
A (min⁻¹)		3.45×10^{12}	6.33×10^{14}	1.41×10^{13}
5% wt. loss for cured sample (°C)	air	436.7	361.2	481.4
	N_2	496.0	383.2	488.2
Residue at 800 °C for cured sample (%)	air	63.6	77.9	51.2
	N_2	79.4	81.5	80.6
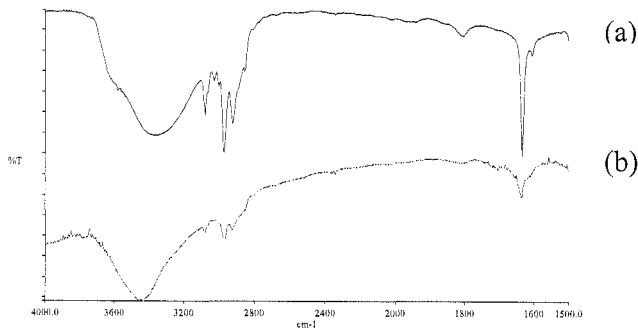
Figure 3: FT - IR spectra of CP-Methyl (a) before DSC scan and (b) after DSC scan

The exothermic transition associated with curing reaction was characterized by noting

the T_p and are given in table 2 at different heating rates. The subsequent heating of these samples showed no traces of any exotherm indicating that the curing reaction was completed in the first DSC scan (fig. 2). The IR spectra of before and after DSC
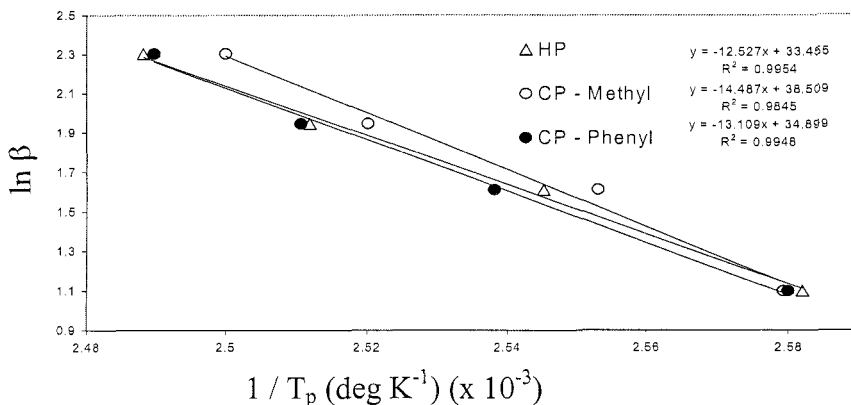

Figure 4: Kinetic plots of LPS based on Ozawa method

scanned samples of **CP-Methyl** had ν_{O-H} peak at about 3400 cm^{-1} which indicates that the hydroxyl end groups do not condense during curing and the exotherm observed in DSC traces was due to the opening of double bond of allyl group as evident by the substantial reduction in the intensity of IR peak at 1627 cm^{-1} (fig. 3). It was obvious from the table 2, that T_p was very much dependent upon the heating rate and increased with increase in heating rate. The heat of curing (ΔH) of **HP** is higher than **CP-Methyl** followed by **CP-Phenyl**, which indicates that ΔH depends on the quantity of the double bonds. In Ozawa's method, E_a was calculated by multiplying $-R/1.052$ with the slope of the plot of ln $[\beta]$ vs. $1/T_p$ (fig. 4) whereas in Kisssinger's method, the slope of the plot of ln $[\beta/T_p2]$ vs. $1/T_p$ (fig. 5) is multiplied with $-R$ to get E_a and the
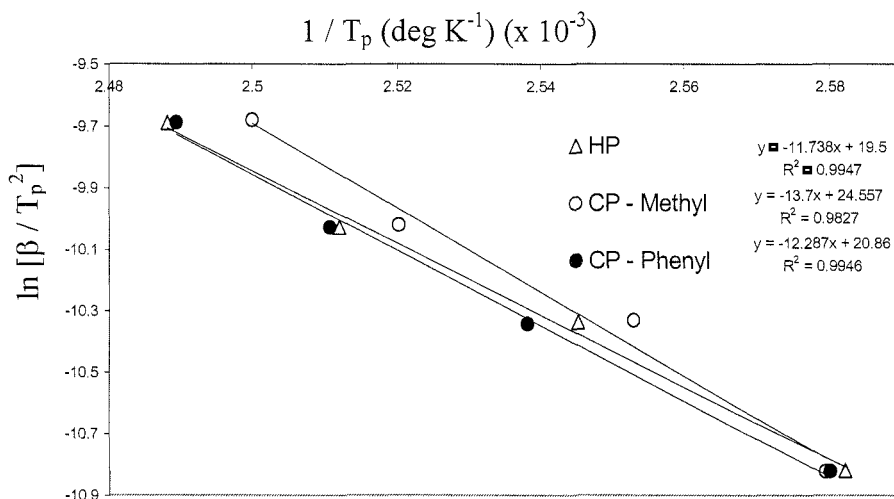

Figure 5: Kinetic plots of LPS based on Kissinger method

values are given in table 2. E_a calculated by both methods is comparable. **HP** was found to have the lowest E_a than copolymers. The dependence of ln A on E_a was found to be linear ($R^2 = 0.9999$) and was not affected by the presence of methyl or phenyl in the place of allyl group.

Thermal stability

LPS was stable up to 300 °C. Uncured **HP** had 5% wt. loss at 305.5 °C whereas cured **HP** at 436.7 °C in air, which suggest that cured samples have higher thermal stability than uncured samples. This is attributed to the formation of cross-linked networks after curing. Thermal stability of LPS was higher in nitrogen than in air. Thermal stability of the cured samples are in the following order: **CP-Phenyl > HP > CP-Methyl**. Residue at 800 °C was higher in nitrogen when compared to air atmosphere.

Conclusions

Three LPSs were successfully synthesized by stepwise coupling polymerization and their characterization data indicated the existence of ladder-like structure with possible defects. Hydroxyl end groups do not condense during curing. Peak maximum temperature increased with increase in the heating rate. Both E_a and A of **HP < CP-Phenyl < CP-Methyl**. Cured **HP** had higher thermal stability than its uncured sample. Thermal stability of the cured samples are in the following order: **CP-Phenyl > HP > CP-Methyl**.

References

1. J. F. Brown Jr, L. H. Vogt Jr, A. Katchman, J. W. Eustance, K. M. Kaiser, and K. W. Krantz, *J. Am. Chem. Soc.*, **82**, 6194 (1960).
2. U. S. 4,826,943 (1989), Oki Electric Industry Co., Ltd, invs.: T. Ito, M. Sakata, and Y. Yamashima.
3. Z. Xie, S. Jin, Y. Wan, and R. Zhang, *Chinese J. Polym. Sci.*, **10**, 361 (1992).
4. Y. Lin, K. P. Pramoda, C. He, W-Y. Chen, and T-S. Chung, *J. Polym. Sci. Part A. Polym. Chem.*, **39**, 2215 (2001).
5. P. S. G. Krishnan, C. He and C. T. S. Shang, *J. Polym. Sci. Part A Polym. Chem.*, **42**, 4036 (2004).
6. P. S. G. Krishnan, and C. He, *Macromol. Chem. Phys.*, **204**, 531 (2003).
7. Liu, C.; Liu, Y.; Xie, P.; Dai, D.; Zhang, R.; He, C.; Chung, T-S. *React. Funct. Polym.*, 2000, **46**, 175-184.
8. Liu, C.; Liu, Y.; Shen, Z.; Xie, P.; Dai, D.; Zhang, R.; He, C.; Chung, T-S. *Macromol. Chem. Phys.*, 2001, **202**, 1576-1580.
9. Wan, Y.; Xu, L.; Ren, L.; Zhang, L.; Xie, P.; Liu, Y.; Zhang, R. *Liq. Cryst.*, 1998, **24**, 871-876.
10. Liu, C.; Liu, Y.; Feng, J.; Yuan, Q.; Xie, P.; Dai, D.; Zhang, R. *React. Funct. Polym.*, 2001, **46**, 213-223.
11. T. J. Ozawa, *J. Therm. Anal.*, **2**, 301 (1970).
12. H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).