

Synthesis and Characterization of Star-shaped Aliphatic Polyester

Young Cheol Shin, Kil-Yeong Choi, and Moon Young Jin*

Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejon 305-600, Korea

Sung-Kwon Hong

Department of Polymer Science and Engineering, Chungnam National University, Taejon 305-764, Korea

Donghyun Cho, Taihyun Chang, and Moonhor Ree

*Department of Chemistry and Center for Integrated Molecular Systems,
Pohang University of Science and Technology, Pohang 790-784, Korea*

Received January 17, 2001

Abstract : Several star-polymers with aliphatic cores were synthesized by ring opening polymerization (ROP) of ϵ -caprolactone using stannous 2-ethyl-hexanoate as a catalyst. The star-polymers were thoroughly analyzed by MALDI-TOF mass spectrometry, temperature gradient interaction chromatography and ^{13}C -NMR to obtain detailed information of the molecular structure. The imperfection of the star-polymers seemed to be originated from restricted participation of sterically hindered hydroxyl groups of initiator. The synthesized star-polymers had narrow molecular weight distributions. Various reaction conditions to control the imperfection were studied.

Introduction

For semiconductor devices with feature sizes below $0.18\ \mu\text{m}$, it is desirable to have materials with a dielectric constant below 2.5 as inter-metallic dielectrics.^{1,2} Several low k materials have been designed and some of them are under-test for application in the semiconductor industry.^{1,2} One of them is a nano-porous organosilicate composed with nano-sized pores and inorganic matrix.³ Nano-pores can be generated by decomposition of nano-separated heat decomposable polymer domains such as poly(ϵ -caprolactone) and poly-alkyl ether, *etc.* In order to control the pore size and the nano-phase separation of the decomposable polymer in inorganic matrix, the molecular structure and its chemical characteristics of pore generating material, porogen, should be well defined in terms of its molecular size, end group and chemical structure. The thermal decomposition

temperature range of porogen is also crucial.⁴

By now, many researchers have reported on the nano-level phase separations of inorganic matrix/organic porogen hybrids, particularly in the molecular composite of silsesquioxanes (SSQs) with thermally degradable polymers that were hyper-branched polyesters⁵⁻⁷ or star-shaped poly(ϵ -caprolactone)s having aromatic cores.⁸⁻¹¹ However, there are few literatures available for accurate structures and detailed thermal properties of porogens. In this report, we present results of synthesis and structural characterizations of new porogens having aliphatic cores and their thermal properties.

Experimental

Materials. Toluene was dried by refluxing over calcium hydride and distilled under nitrogen prior to use. The ϵ -caprolactone (b.p. = $96^\circ\text{C}/10\ \text{mmHg}$) was dried over calcium hydride, distilled under pressure, and stored under nitrogen atmosphere. The trimethylol propane, di(trimethylol propane)

*e-mail : myjin@kRICT.re.kr

and di(pentaerythritol) obtained from Aldrich were recrystallized from acetone and then dried for 24 hrs at 30°C under pressure. All other chemicals and solvents were extra-pure grade and used without further purification.

Polymerization. For the preparation of 4 arm star-polymer, ϵ -caprolactone was added to flame-dried flask containing di(trimethylol propane) used as a initiator adjusting molar ratio (monomer to initiator) for target Avg.DPn/arm. The flask was heated to 110°C where ϵ -caprolactone dissolved the initiator forming a homogeneous solution. Then, the stannous 2-ethyl-hexanoate (1/200 of mol. of initiator) was added to flask and the reaction was maintained at 110°C for 20 hrs. The polymers were dissolved in THF and precipitated into cold methanol.

¹H-NMR (CDCl₃) of 3 arm star-polymer : δ (ppm) 0.89 (t, 3H), 1.35-1.44 (m, 2H), 1.61-1.70 (m, 4H), 2.31 (t, 2H), 3.63 (t, 2H), 4.02 (s, 2H), 4.06 (t, 2H); ¹³C-NMR (CDCl₃) : δ (ppm) 7.71, 23.26, 24.87, 25.83, 28.65, 32.63, 34.42, 41.00, 62.75, 64.46, 173.90

¹H-NMR (CDCl₃) of 4 arm star-polymer : δ (ppm) 0.87 (t, 3H), 1.35-1.43 (m, 2H), 1.60-1.70 (m, 4H), 2.31 (t, 2H), 3.28 (s, 2H), 3.64 (t, 2H), 4.02 (s, 2H), 4.06 (t, 2H); ¹³C-NMR (CDCl₃) : δ (ppm) 7.70, 23.27, 24.82, 25.78, 28.59, 32.58, 34.37, 41.84, 62.61, 64.40, 71.24, 173.82

¹H-NMR (CDCl₃) of 6 arm star-polymer : δ (ppm) 1.37-1.44 (m, 2H), 1.60-1.68 (m, 4H), 2.31 (t, 2H), 3.28 (s, 2H), 3.62 (t, 2H), 4.02 (s, 2H), 4.06 (t, 2H); ¹³C-NMR (CDCl₃) : δ (ppm) 24.78, 25.59, 28.55, 32.55, 34.30, 43.15, 62.49, 64.33, 71.14, 173.73

Model Compound. Di(trimethylol propane)

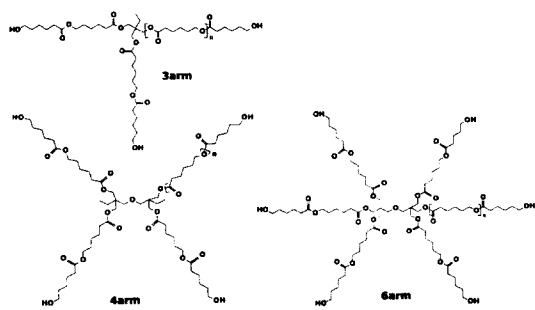


Figure 1. Structures of synthesized star-polymers.

(0.794 g, 3.17 mmol) in THF (20 mL) and pyridine (0.752 g, 9.51 mmol) were added to flask, and then hexanoyl chloride (1.28 g, 9.51 mmol) was dropped into flask at 0°C. After 1 hr, the temperature was raised to 25°C, and maintained for 1 hr. As the reaction was completed, the solvent was removed, and the collected residues were purified by column chromatography on silica (eluent : hexane/ethyl acetate, 1/1, v/v).

Modification of Terminal Functional Groups. Hydroxyl terminated 4 arm star-polymer (5.00 g, 1.88 mmol) in THF (50 mL) and pyridine (5.95 g, 75.2 mmol) were added to flask, and then acetyl chloride (5.90 g, 75.2 mmol) or ethyl chloroformate (8.16 g, 75.2 mmol) was dropped into flask at 0°C. After 1 hr, the temperature was raised to 25°C, and maintained for 1 hr. The reaction solution was poured into methanol/water (1/1, v/v, 500 mL) and precipitated.

Measurements. ¹H-NMR and ¹³C-NMR spectra were recorded with a Bruker AMX 300MHz spectrometer using CDCl₃ as a solvent. Gel permeation chromatography (GPC) measurements were carried out at 40°C using THF as an eluent at a flow rate of 1.0 mL/min, and chromatograms were calibrated with polystyrene standard. Molecular weight of each star-polymer was measured using PerSeptive Biosystem-Voyager-DE-STR MALDI-TOF (matrix assistance laser desorption ionization time of flight) mass spectrometer equipped with a nitrogen laser 337 nm in deflected mode, where DHB (dihydroxybenzoic acid) as a matrix and NaI as a accelerating cationic ion were used. TGIC (temperature gradient interaction chromatography) equipped with a C18 bonded silica column (Phenomenex, LUNA C18, 250×4.6 mm ID) was utilized to identify structural isomerism. The column temperature was varied from 25 to 65°C with a heating rate of 1.5°C/min, and acetonitrile was used as an eluent at a flow rate of 0.5 mL/min. Normal phase HPLC (NPLC) equipped with a bare silica column (Alltech, Nucleosil, 250×4.6 mm ID) was also used to identify structural isomerism at 25°C, where i-octane/THF (45/55, v/v) mixture was used as an eluent at a flow rate of 0.5 mL/min. Thermal properties were measured by TA instruments 2950 thermogravimetric analyzer (TGA), TA instruments 2910 differential

scanning calorimeter (DSC) and Nicolet MAGNA-IR 560 TGA-IR spectrometer with a heating rate of 10 °C/min in nitrogen atmosphere.

Results and Discussion

Structural Analysis. The porogens, star-polymers, were synthesized by ring opening polymerization (ROP) of ϵ -caprolactone using stannous 2-ethyl-hexanoate as a catalyst. The cores of the star-polymers were selected from aliphatic multi-armed polyols such as trimethylol propane, di(trimethylol propane) and di(pentaerythritol) for 3, 4, and 6 arm star-polymers, respectively. It is well known that ϵ -caprolactone can be polymerized as a manner of pseudo-living polymerization by the initiation of hydroxyl group under these conditions. In this work, the targeted degrees of polymerization for each arm were selected to 6, 8, 10 and 12, which were controlled by adjusting the molar ratio of monomer to initiator. The polymerization results of synthesized star-polymers (PORO) are shown in Table I.

The number average molecular weight (M_n) and molecular weight distribution (MWD) of star-polymers were determined by MALDI-TOF, GPC and end group analysis of $^1\text{H-NMR}$ spectrum. As summarized in Table I, the degree of polymerization (DP) had good agreement with the monomer to initiator ratio and the polydispersity was nar-

row (1.04~1.09).

MALDI-TOF is one of the powerful analytical tools for determining the molecular weight (M_w) of each polymer molecule.¹²⁻¹⁴ Figure 2 shows the typical MALDI-TOF mass spectroscopy of 4 arm star-polymers and each peak represents a mass of star-shaped polymer molecule with sodium ion adduct. The DP_n of the 4 arm star-polymer can be calculated using the following equation.

$$\text{Mass (m/z)} = 114.14 (M_w \text{ of } \epsilon\text{-caprolactone}) \times \text{DP}_n + 250.34 (\text{initiated core}) + 23 (\text{sodium ion}).$$

For example, the highest peak in the spectrum of the typical 4 arm star-polymer (PORO4-5, Fig-

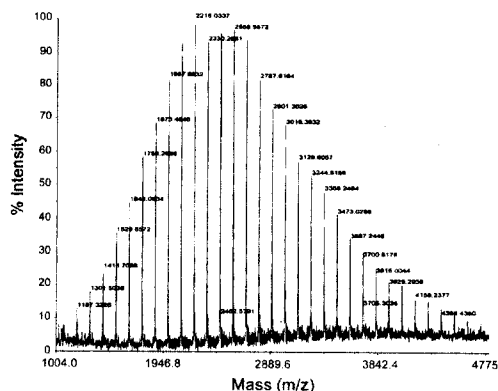


Figure 2. MALDI-TOF spectrum of typical 4 arm star-polymer.

Table I. Characteristics of Synthesized Star-polymers

PORO : No of arm-Avg. DP _n /arm	M_n (g/mol) ^a	DP _n	MWD	TDI (°C) ^b	TDT (°C) ^b
PORO3-6	2,589	21.3	1.06	234	395
PORO3-8	3,223	26.8	1.06	285	420
PORO3-10	3,469	29.0	1.06	220	365
PORO3-12	3,610	30.4	1.08	270	430
PORO4-5	2,448	19.0	1.07	229	397
PORO4-6	3,014	24.0	1.04	220	402
PORO4-8	3,841	31.3	1.08	233	410
PORO4-10	4,348	35.7	1.09	234	386
PORO4-12	5,224	43.4	1.08	224	382
PORO6-6	4,171	34.1	1.09	220	405
PORO6-8	5,480	45.6	1.07	270	405

^aCalculated from MALDI-TOF spectrum.

^bTDI : Initial thermal degradation temperature, TDT : Terminal thermal degradation, Temperature acquired from TGA thermogram.

ure 2) showed a mass of 2,452.57 g/mol, which represents 19 mers of ϵ -caprolactone monomers associated with di(trimethylol propane) as a core.

The presence of a single set of peaks in MALDI-TOF spectroscopy provides strong support for the existence of only one kind of polymeric species in the system. It means no other initiation sources except the core material are present in the star-polymers.

Since the interaction of the porogen and the matrix is one of the most important factors to get a nano-separated system, the information of the molecular structure and its irregularity of star-polymer are the major interesting subjects to concern. As shown in Figure 2, the broad spectrum of star-polymers with different Mw were present, ranged from 8 to 39 mer, even the calculated MWD was only 1.06. Since an oligomer with only 8 degree of polymerization is very short to form a star-shaped structure with $DP_{arm} = 2$ for each four arms, it is very reasonable to speculate that the star-polymers with different chemical structures are present including imperfect 2 or 3 armed star-polymers. The presence of the imperfect star-polymers may strongly influence on the nano-phase separation, if they existed.

At this moment we have to consider the limitation of performance of the analytical tools. In fact, the MALDI-TOF could not distinguish detailed structural differences of oligomer, it only gave us Mw of each molecule, e.g. how many monomers are incorporated in the star-polymer, regardless of

how the monomers are incorporated. And, the GPC gave rather crude information on the molecular weight of star-polymer due to its low resolution. But, interaction chromatography gives us more detailed information on the molecular imperfection of multi-armed star-polymer.¹⁵⁻¹⁸ Figure 3 showed the chromatograms of PORO4-8 obtained by (a) TGIC using a reversed stationary phase and (b) NPLC using a bare silica column.

As can be seen in Figure 3, two separated envelopes are recognized from TGIC and NPLC, even though the experiments of MALDI-TOF and GPC showed that the star-polymers seemed to be composed of single family. The TGIC chromatogram of the star-polymer (Figure 3(a)) revealed a fine structure and the individual peak correspond to a different DP of ϵ -caprolactone units. The two envelopes arose from slight mismatch of the peak positions. The major envelope appeared at ca. 30 min and the other envelope showed that ca. 23 min in retention time. If the two different envelopes were due to the different number of arms, it would be better resolved by NPLC, which is more sensitive to the polar end groups. As expected, the NPLC chromatogram (Figure 3(b)) showed a better resolved chromatogram indicating the presence of materials with different molecular architectures in PORO4-8. This would be the first example that there are different kinds of star-polymers in the ring-opening polymerized multi-armed star-polymers.

To identify the detailed chemical structure of

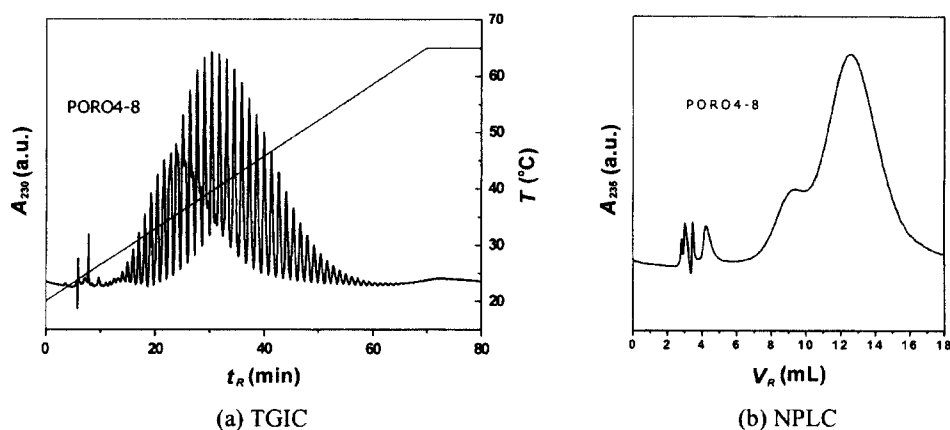


Figure 3. Chromatograms of PORO4-8.

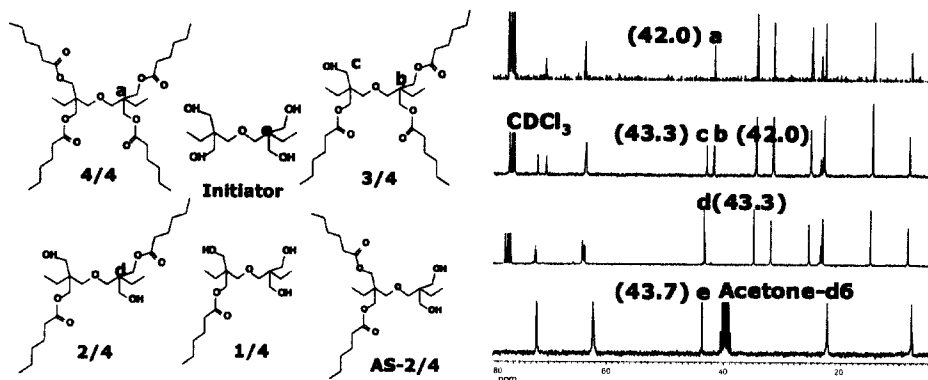


Figure 4. Structures and ^{13}C -NMR spectra of model compounds.

the isomeric star-polymers mixture, we have synthesized the three model compounds (Figure 4) which were prepared with the 4 arm initiator and hexanoyl chloride, and analyzed the separated compounds by using ^{13}C -NMR.

As shown Figure 4, the tertiary carbon peak of the model compound (4/4 structure) with fully substituted showed up at 42.0 ppm (a), and the carbon of 3/4 structure having one unsubstituted methylol group appeared at 42.0 ppm (b) and 43.3 ppm (c). And the carbon of 2/4 structure with two methylol group was located at 43.3 ppm (d), and ^{13}C -NMR chemical shift for the tertiary carbon of the di(trimethylol propane) as a 4 arm initiator was 43.7 ppm (e).

As can be compared with expanded ^{13}C -NMR spectra of the star-polymers (Figure 5), we certainly realized that the synthesized star-polymers didn't have a single structure. The ^{13}C -NMR of the star-polymers of this study showed two distinguishable ^{13}C -NMR peaks located at 41.9 and 43.1 ppm including small peaks at shoulders. Thus, it can be concluded that there are three different, at least, analogs of star-polymers. They are the perfect star-polymers with 4 armed and two imperfect ones, 3/4 star-polymer (similar to 3/4 of Figure 4, which has regular three arms and one imperfect arm) and small portion of 2/4 star-polymer (similar to 2/4 of Figure 4, regular two arms and two imperfect arms). We could excluded that the analogs of AS-2/4 star-polymer and 1/4 star-polymer initiated only one side of core molecules (Figure 4) since the chemical shift of the tertiary carbon

should be located on 43.7 ppm as can be seen from the ^{13}C -NMR of the starting material. From the comparison of ^{13}C -NMR intensity, TGIC and NPLC, we concluded that the major envelopes of TGIC and NPLC are attributed to perfect 4 arm and the small envelope is belong to analog of 3/4 structure. This result clearly demonstrates that the reactivity of growing hydroxyl chain end in star-shaped molecules is different to that of the hydroxyl group of the initiator. Once a monomer insert to a certain hydroxyl group of the initiator, the adjacent hydroxyl group of the initiator has a steric hindrance, and the coordination-insertion mechanism might be impeded for the "buried" hydroxyl group. An increase of the steric hindrance for these sites leads to asymmetric and imperfect chemical structure of the star-polymers.

In order to control the factor for assymetric and imperfect initiations of ROP, we have examined various factors for reaction conditions. It was found that the structural imperfection was significantly dependent on the reaction temperature and the agitation rate, as shown ^{13}C -NMR spectra in Figure 5, and we observed that the lower temperature and higher speed of agitation are favorable to get a better architectural perfectness of star-polymers. Which implied that the polymerization depends on the diffusion rate of monomer to the hydroxyl group of core.

Thermal Properties. The understanding of thermal properties of star-polymer for a nanoporous material is very important. The star-polymer should start to decompose after matrix material

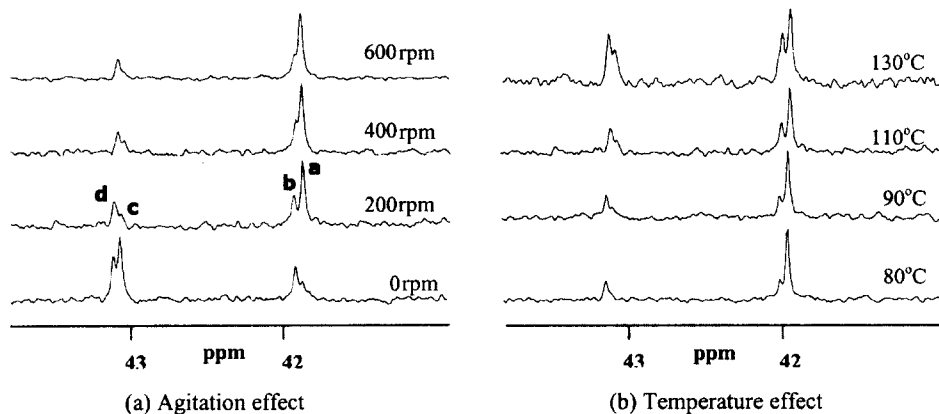


Figure 5. The expanded ^{13}C -NMR spectra of PORO4-6.

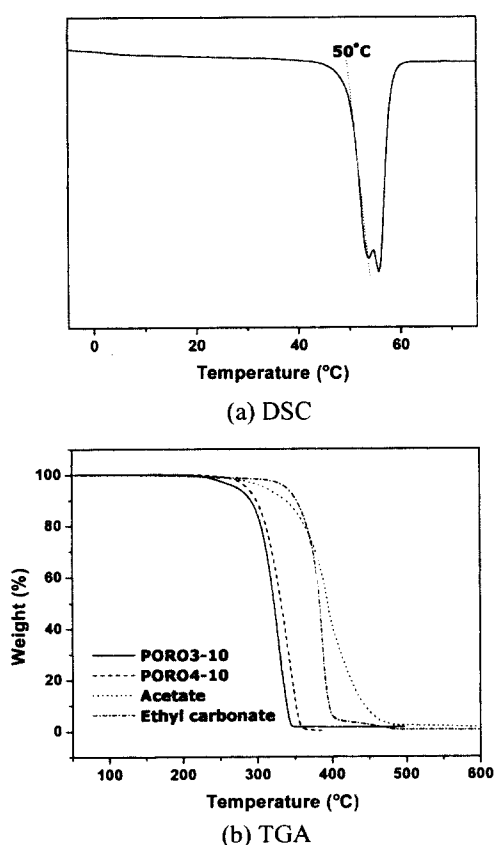


Figure 6. Thermograms of various star-polymers.

has been cured to retain the nano-porosity, and its decomposition should be complete before the matrix has been degraded. It is known that the

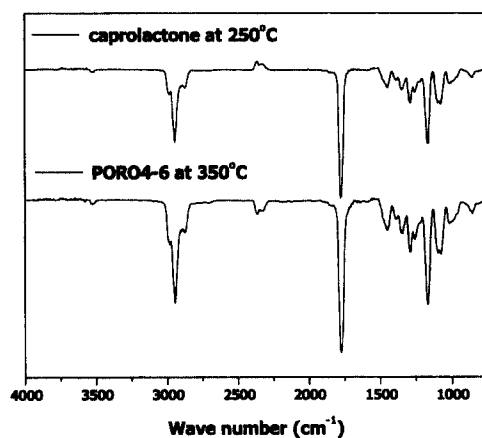
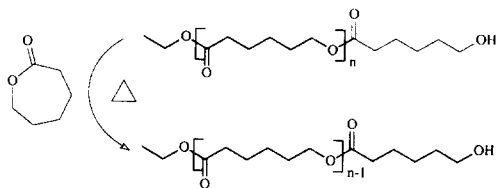


Figure 7. TGA-IR spectrum of PORO4-6.

matrix of the MSSQ is cured above 200°C and decomposed at 420°C . Thermal properties of star-polymers were characterized by TGA, DSC and TGA-IR. All the synthesized star-polymers showed the melting transition near 50°C as shown in Figure 6(a), and were completely decomposed range from 200 to 430°C . For instant, the initial decomposition temperature and the terminal decomposition temperature of PORO4-10 is 234°C and 386°C , respectively, as shown in Figure 6(b) and Table I. The decomposition range was very proper to form a nano-porous organo-silicate.

We have also investigated the decomposition mechanism of the star-polymers by utilizing TGA-IR. As can be seen from Figure 7, the IR peak of the decomposed vapor at 350°C was exactly



Scheme I. Unzipping mechanism of star-polymer degradation.

Table II. TGA Results of Modified Star-polymers

Target	TDI(°C)	TDT(°C)
PORO4-6	220	402
Acetate	247	483
Ethyl carbonated	243	474

matched to that of the ϵ -caprolactone vapor at 250°C. The results of TGA-IR suggested that the decomposition of the star-polymer was proceeded via unzipping mechanism, the star-polymer starts to decompose from the end of chain (Scheme I).

To support the unzipping mechanism, we synthesized and analyzed various star-polymers, in which the hydroxyl end groups were blocked with other functional group, such as acetate and carbonate. The decomposition of the modified star-polymer is shown in Table II and TGA thermogram is shown in Figure 6(b).

The star-polymer having acetyl or carbonate end group showed a higher degradation temperature, compared to star-polymers having hydroxyl functional group. Thus, the initiation of degradation via unzipping is slightly hindered by the modified end group.

Acknowledgement. This work was supported by the Korea Collaborative Project for Excellence in Basic System IC Technology(99-B4-C0-00-01-00-02). TC and MR acknowledge the support from BK21 program.

References

- (1) L. Peters, *Semiconductor International Sept.*, 64 (1998).
- (2) *MRS Bulletin*, **22**, 19 (1997).
- (3) J. L. Hedrick, R. D. Miller, C. J. Hawker, K. R. Cater, W. Volksen, D. Y. Yoon, and M. Trollsas, *Adv. Mater.*, **10**, 1049 (1998).
- (4) J. L. Hedrick, R. D. Miller, C. J. Hawker, R. Twieg, S. A. Srinivasan, and M. Trollsas, *Macromolecules*, **30**, 7607 (1998).
- (5) C. Nguyen, C. J. Hawker, R. D. Miller, E. Huang, J. L. Hedrick, R. Gauderon, and J. G. Hillborn, *Macromolecules*, **33**, 4281 (2000).
- (6) E. Malmstrom, M. Johansson, and A. Hult, *Macromolecules*, **28**, 1698 (1995).
- (7) H. Ihre, A. Hult, and E. Soderlind, *J. Am. Chem. Soc.*, **118**, 6388 (1996).
- (8) J. F. Remenar, J. L. Hedrick, R. D. Miller, C. J. Hawker, D. Y. Yoon, S. M. Kim, and M. Trollsas, *Polymer Preprint*, **38**, 631 (1998).
- (9) M. Trollsas and J. L. Hedrick, *J. Am. Chem. Soc.*, **120**, 4644 (1998).
- (10) M. Trollsas, J. L. Hedrick, D. Mecerreyes, P. Dubios, R. Jerome, H. Ihre, and A. Hult, *Macromolecules*, **31**, 2756 (1998).
- (11) C. V. Nguyen, K. R. Cater, C. J. Hawker, J. L. Hedrick, R. L. Jaffe, R. D. Miller, J. F. Remenar, H. W. Rhee, P. M. Rice, M. F. Toney, M. Trollsas, and D. Y. Yoon, *Chem. Mater.*, **11**, 3080 (1999).
- (12) A. K. Chaudhary, G. Critchley, A. Diaf, E. J. Beckman, and A. J. Russell, *Macromolecules*, **29**, 2213 (1996).
- (13) D. Yu, N. Vladimirov, and J. M. J. Frechet, *Macromolecules*, **32**, 5186 (1999).
- (14) G. Montaudo, M. S. Montaudo, C. Puglisi, and F. Samperi, *Macromolecules*, **28**, 4562 (1995).
- (15) H. C. Lee, W. Lee, T. Chang, J. S. Yoon, D. J. Frater, and J. W. Mays, *Macromolecules*, **31**, 4114 (1998).
- (16) H. C. Lee, T. Chang, S. Harville, and J. W. Mays, *Macromolecules*, **31**, 690 (1998).
- (17) T. Chang, H. C. Lee, W. Lee, S. Park, and C. Ko, *Macromol. Chem. Phys.*, **200**, 2188 (1999).
- (18) H. C. Lee, W. Lee, and T. Chang, *Korea Polym. J.*, **4**, 160 (1996).