Polymer Bulletin 35, 423-430 (1995)

Polymer Bulletin

Synthesis, characterization and properties of polyimides from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and imidazole-blocked 2,5-bis[(*n*-alkyloxy)methyl]-1,4-benzenediisocyanates

Jin Chul Jung *, **Sang-Bong Park**

Department of Materials Science and Engineering, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang, 790-784 Korea

Received: 17 April 1995/Revised version: 22 May 1995/Accepted: 30 May 1995

Summary

By the solution condensation of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) with imidazole-blocked 2,5-bis[(n-alkyloxy)methyl]-1,4-benzenediisocyanates (C_m-BDIs) a series of aromatic polyimides (C_m-BP-PIs) having flexible (n-alkyoxy)methyl ($-CH_2O-n-C_mH_{2m+1}$, m = 4, 6, 8) side chains were prepared and characterized by IR- and ^{1}H-NMR spectroscopy and their properties were measured and discussed in respect to the effects of side chains. Inherent viscosities of the polymers were in the 0.23 - 0.34 dL/g range. All the polymers were highly soluble in N,N'-dimethylpropyleneura(DMPU) and C_6- and C_8-BP-PIs even in $CHCl_3$ at room temperature. UV-VIS spectra showed that the π-electrons are delocalized along the main chain. TGA studies showed a two-step pyrolysis behavior and in DSC Tg's of C_4-, C_6- and C_8-BP-PIs were determined to be 184, 135 and 127 ℃, respectively. Wide-angle X-ray diffractometry for as-polymerized samples revealed a quite low crystallinity with only loosely developed layered structure.

Introduction

Aromatic polyimides derived from BTDA are certainly an important class of high-performance thermoplastics(1-3) with excellent thermal stability. These polyimides have mainly been developed for the purpose of higher processability and deformation properties than the corresponding polyimides derived from pyromellitic dianhydride(2). These propertiy improvements are achieved by insertion of C=O group between the two benzene rings of dianhydride segments of the polymer chain. Properties of aromatic BTDA-polyimides are, of course, governed also by structure of aromatic diamine units incorporated. In spite of the presence of a kinked C=O link, the polyimide prepared from BTDA and p-phenylenediamine has such a highly rigid backbone that it is not soluble in any common organic solvents and no T_g has been determined yet(4).

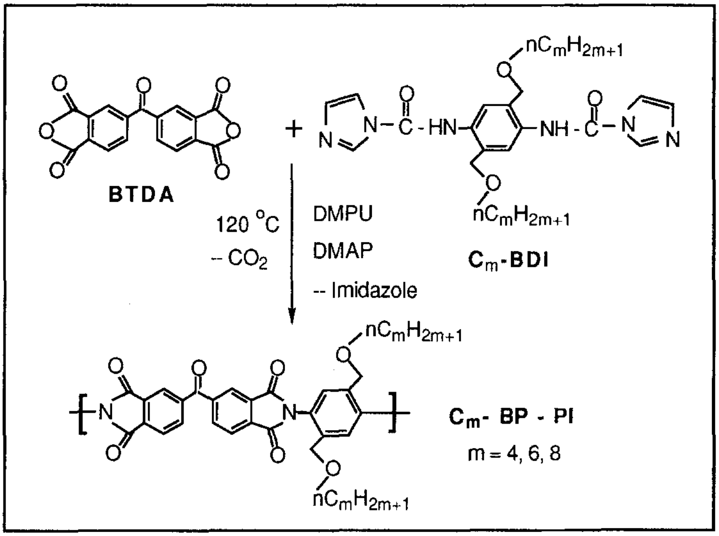
To dramatically improve solubility and fusibility of stiff-chain polymers, a method of appending long, flexible side chains to rigid main chains has recently been introduced(5,6) and a number of wholly aromatic polyimides having n-alkyl(7), n-alkyoxy(8) or poly(ethyleneoxy)(9) side chains have been synthesized. These polymers were found to be highly soluble in polar solvents such as N-methyl-

---

* Corresponding author

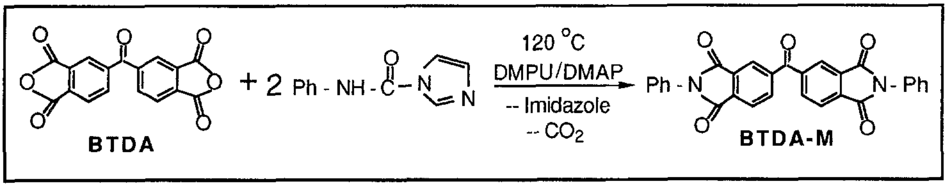
pyrrolidone, dimethyl sulfoxide (DMSO) or dimethyl acetamide(DMAc) and to form a unique layered crystalline structure in their solid states.

The purpose of the present study is to enhance solubility and fusibility of the polyimide derived from BTDA and p-phenylenediamine by means of appending (n-alkyloxy)methyl side chains with various chain lengths. The appendance of side chains also aims at investigating its effects on formation of layered structure and properties of the polyimides. It was achieved by the condensation of imidazole-blocked 2,5-bis[(n-alkyloxy)methyl]-1,4-benzenediisocyanates (C_m-BDIs, m = 4, 6, 8) with BTDA in DMPU solution in the presence of 4-N,N-dimethylamino-pyridine (DMAP) catalyst at 120 °C, as shown in Scheme 1.



Scheme 1. Synthesis of C_m-BP-PIs.

To get a better understanding on the polymerization reaction and characterization of the polymers, a model compound N,N'-diphenylbenzophenonetetracarboxylic diimide (BTDA-M) was prepared from the condensation of N-(1-imidazolylcarbonyl)aniline with BTDA under the same reaction conditions as in the polymerization, as shown in Scheme 2.



Scheme 2. Synthesis of model compound BTDA-M.

Experiment

Chemicals. N-(1-imidazolylcarbonyl)aniline was prepared according to a literature

(8). Pure BTDA was obtained by recrystalization from acetic anhydride. DMPU was purified by vacuum distillation over CaH_2. DMAc, DMSO and toluene were made pure by usual methods. Imidazole, DMAP, ethyl chloroformate and other reagents were used as received.

Measurements. IR spectra were taken from a Shimadzu FT-IR 4300 in KBr pellets. Elemental analyses were made by a Carlo Erba EA microanalyzer. DSC measurements were made from a Perkin-Elmer PEPC Series DSC 7 and TGA thermograms were taken from a Perkin-Elmer Delta Series TGA 7, both at a heating rate of 10 °C/min under N_2. Wide-angle X-ray diffractograms were taken in reflection mode using a Ni-filtered CuKα radiation on a Rigaku Geiger Flex D-Max. UV-VIS spectra were obtained in concentrated sulfuric acid solution using a Hewlett Packard 8452A Diode Array Spectrometer. Inherent viscosities were measured from 0.2 g/dL DMPU solutions at 25 °C.

Monomer synthesis. Monomeric C_m-BDIs were synthesized from 2,5-bis[(n-alkyloxy)methyl)-1,4-benzenedicarboxylic acids, which had been prepared from p-xylene according to our previous papers(10,11). The diacids were converted to diacid chlorides by reaction with ethyl chloroformate(12) in a mixture from DMSO/DMAc (2/7 v/v) at 0 °C. When the diacid chlorides were further reacted with NaN_3 in the presence of excess toluene, diacid azides were formed(13), which were readily converted to C_m-BDIs by heating the reaction mixtures in the presence of excess imidazole(14). C_m-BDIs were purified by recrystallization from acetone. Detailed procedure for the synthesis and characterization data of the monomers will be published elsewhere(15).

Preparation of BTDA-M. To a 150 mL round-bottomed flask equipped with a reflux condenser, a stirrer and a drying tube were placed 20 mmol of N-(1-imidazolylcarbonyl)-aniline, 10 mmol of BTDA and 1.4 mmol of DMAP diluted in 60 mL of DMPU and the mixture was stirred at 95 °C in N_2 atmosphere till the end of CO_2 evolution. After cooled to room temperature, it was poured into 200 mL ethanol. The precipitates formed were collected and purified by recrystallization from ethanol.

Yield: 49 %. m.p.: 358 °C(DSC). IR in cm^{-1}: 1780 & 1720 (imide I), 1655 (C=O), 1394 & 1380 (imide II), 1138 (imide III) and 714 (imide IV). Analysis calc. for $C_{29}H_{16}N_2O_5$ in wt. %: C 73.73, H 3.41, N 5.93 and O 16.93 and found: C 71.72, H 3.37, N 5.85 and O 19.36.

Synthesis of C_m-BP-PIs. To a 150 mL round-bottomed flask equipped with a reflux condenser and drying tube were placed 6 mmol of a C_m-BDI, 6 mmol of BTDA and 0.84 mmol of DMAP dissolved in 20 mL of DMPU under N_2. The solution was heated to 120 °C and stirred for two days in N_2 atmosphere till the end CO_2 evolution, whereby additional 20 mL of DMPU were dropped in to reduce the solution viscosity. At the end of polymerization reaction the polymer was isolated by precipitation from excess ethanol and purified by reprecipitation of $CHCl_3$ solution from ethanol. Pure polymer was obtained by extracting with acetone and drying in vacuum at 70 °C to a constant weight. Yields were found to be nearly quantitative in all polymerizations.

Results and discussion

Synthesis. Although the polyimide derived from BTDA and p-phenylenediamine contains a kinked C=O unit in its repeat unit, it is still so rigid that it is insoluble in any common organic solvents and its T_g is not meausrable at all. To obtain a soluble polyimide having the same backbone structure, a series of new polyimides were synthesized by the condensation of BTDA with three C_m-BDIs having various (n-alkyloxy)methyl side chain lengths. This polymerization accompanies CO_2 evolution and is a one-step reaction leading directly to imidized polymers(8), and the degree of reaction could readily be traced by measuring the volume of CO_2 evolved. When polymerization reactions were stopped at the end of CO_2 evolution, it could be confirmed that the reaction had proceeded almost quantitatively.

During the whole polymerization reactions the systems remained completely homogeneous, when additional DMPU was dropped into the system. This homogeniety might help obtain the quantitative polymerization yields. To completely remove imidazole byproduced, the polymers needed be thoroughly purified by reprecipitation from chloroform/ethanol solvent pair followed by extraction with acetone.

Characterization. In comparison with BTDA-M, the polymers obtained were characterized by IR and ^{1}H-NMR spectroscopy. In Figure 1 is reproduced the IR spectrum of C_8-BP-PI together with that of BTDA-M. From Figure 1 it is to see that the IR absorption peaks arising from imide I, II, III and IV and C=O vibrations of C_8-BP-PI are readily detectable at 1780 and 1724 , 1354, 1102 and 723 and 1670 cm^{-1}, respectively, although at 1102 and 723 cm^{-1} the respective C-O-C and $(CH_2)_4$ vibrations appear overlapped. In addition, in C_8-BP-PI C-H stretching vibrations are observed in the 2855 - 1960 cm^{-1} range. The other C_4- and C_6-BP-PIs revealed the same IR absorption characteristics as C_8-BP-PI. These IR spectroscopic characterizations indicate that the polymers prepared have the same structure as expected.

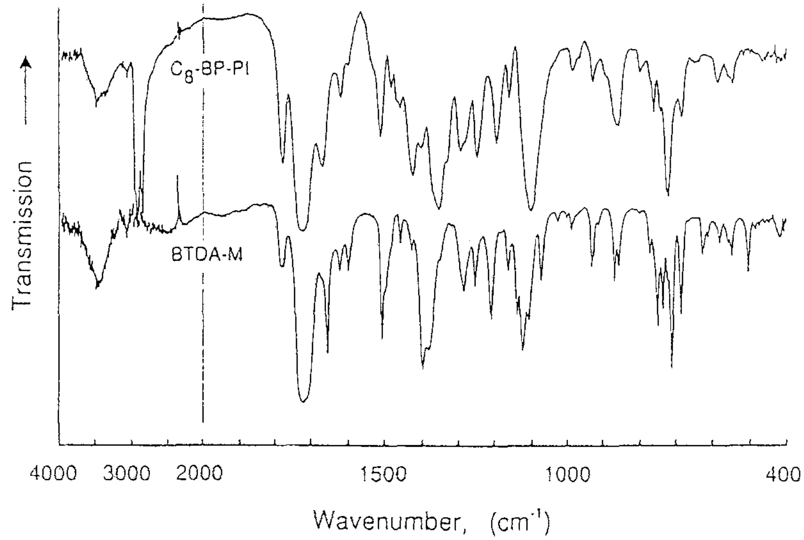


Figure 1. IR spectra of C_8-BP-PI and BTDA-M.

In Figure 2 is reproduced the ^{1}H-NMR spectrum of C_6-BP-PI taken in $CDCl_3$ at room temperature. Based on ^{1}H-NMR data of model compound BTDA-M all the peaks could be satisfactorily interpretated and this interpretation is indicated in Figure 2. ^{1}H-NMR spectrum of C_4-BP-PI could not be taken due to low solubility in chloroform. But C_8-BP-PI could be so clearly interpretated as C_6-BP-PI, and it may be believed that the polymers were satisfactorily prepared.

Properties. In Table I are summarized the solution properties of C_m-BP-PIs thus

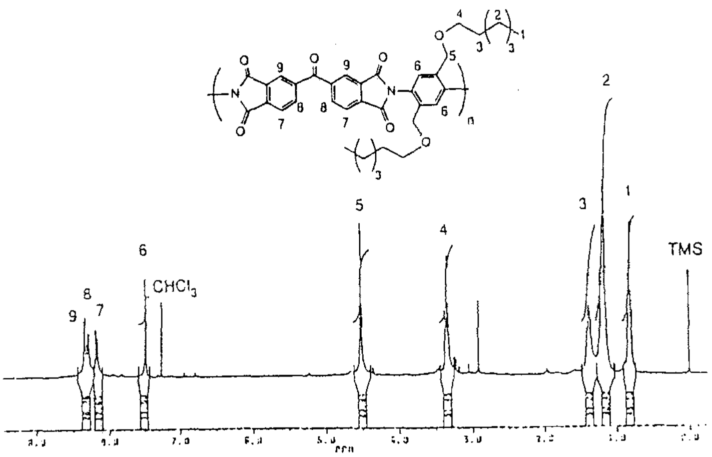


Figure 2. ^{1}H-NMR spectrum of C_6-BP-PI.

synthesized. Table I shows that inherent viscosities of the polymers lie in the 0.23 - 0.34 dL/g range and even C_4-BP-PI having the shortest side chain length is highly soluble in an aprotic solvent DMPU at room temperature and on heating it is slighly soluble in chloroform. With increasing side chain length solubility of the polymers increases so much that C_6- and C_8-BP-PIs are highly soluble even in chloroform at room temperature. Remarkable increase in solubility with increasing side chain length is understandable from the viewpoint of bound-solvent action of side chains toward rigid main chains(5).

Table I. Solution properties of C_m-BP-PIs.

Polymer code	η_{inh} (dL/g)	Solubility				
		DMAc	DMPU	H_2SO_4	CH_3SO_3H	$CHCl_3$
C_4-BP-PI	0.23	+	+++	+++	+++	+[a]
C_6-BP-PI	0.33	+++	+++	+++	+++	+++
C_8-BP-PI	0.34	+++	+++	+++	+++	+++

a) Soluble upon heating.
+ slightly soluble, +++ soluble at room temperature.

Rigidity of aromatic main chain originates from an interchain attraction among rod-like aromatic segments. With increasing length of the resonance-stabilized π-electron system the rod length and hence the attractive interaction naturally increase. To study main chain rigidity of C_m-BP-PIs, extension of the π-electron delocalization along their main chains was investigated by UV-VIS spectroscopy. In Figure 3 are reproduced the UV-VIS spectra of C_m-BP-PIs together with that of BTDA-M. Figure 3 shows that the absorption maxima of C_m-BP-PIs arising from π - π* transition clearly appear at longer wavelengths than the maximum of BDTA-M. This behavior indicates that π-electron resonance system is more or less extended along the main chain axis, although C=O link is not linear but about 60° bent. This means that contribution of the conformation, in which the two benzene rings linked to

C=O group come onto the same plane, is fairly high. This extended delocalization is believed to render main chain of the polyimide from BTDA and p-phenylenediamine so stiff that it is not soluble in any organic solvents.

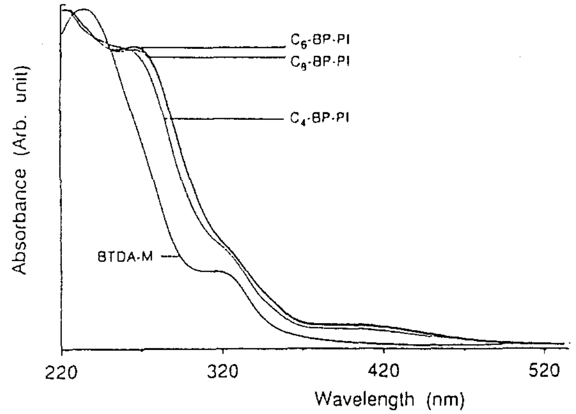


Figure 3. UV-VIS spectra of C_m-BP-PIs and BTDA-M.

The thermal resistance of C_m-BP-PIs was investigated by TGA in N_2. In Figure 4 the thermal pyrograms are reproduced and the numerical values obtained from the curves are summarized in Table II. As Figure 4 shows, with elevation in temperature all the C_m-BP-PIs take a two-step reaction mode. In the lower-temperature range the side chains split out and in the higher-temperature range the main chains decompose. This behavior is evidenced by the result shown in Table II. It reveals that the measured Ws(B) values coincide quite well with the calculated Ws(B) values within experimental error.

Table II. Thermal pyrolysis behavior of C_m-BP-PIs in N_2.

Polym. code	1st. T_i (°C)	2nd. T_i (°C)	WR_{800} (wt %)	Ws in wt %		ΔWs (A - B)
				Calculated(A)	Observed (B)	
C_4-BP-PI	384	570	47	31	33	2
C_6-BP-PI	383	568	44	37	39	2
C_8-BP-PI	389	572	42	42	43	1

Ti: On-set temperature of degradation.
WR_{800} : Weight remained at 800 °C.
Ws(A): Wt. % of side chain contained.
Ws(B) : Wt. % degraded away in the lower-temperature range.

This two-step pyrolysis behavior indicates that in spite of the presence of flexible side chains the main chain of C_m-BP-PIs is still so rigid that the internal plasticizer action of side chains toward main chains are not sufficiently high, presumably because side chain length is not sufficiently long. Table II also shows that 2nd. T_i is independent of side chain length. This is natural to understand, since after split-out of side chains from any C_m-BP-PIs the same backbone structure as the polyimide derived from BTDA and p-phenylenediamine is obtained.

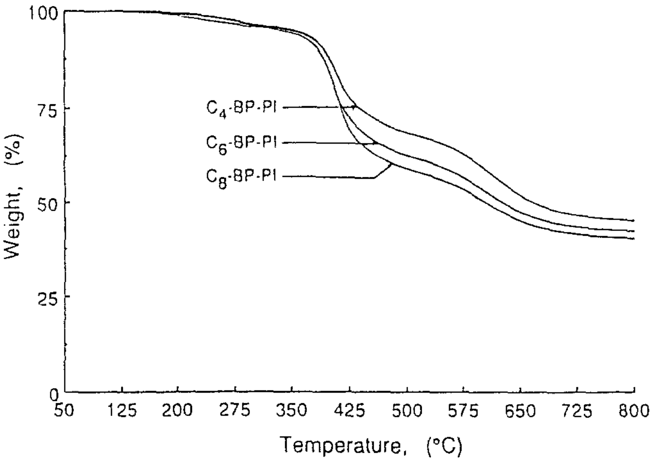


Figure 4. Thermal pyrograms of C_m-BP-PIs in N_2.

Crystalline structure of as-polymerized powder C_m-BP-PIs was determined by wide-angle X-ray diffraction. In Figure 5 are reproduced the X-ray diffractograms. As Figure 5 shows, the reflections are generally so broad that crystallinity of the samples must be quite low. The reflections characteristic of layer spacing of the layered crystalline structure appear in small-angle region, but they are also so broad that layered structures of C_m-BP-PIs must be only loosely developed, and any quantitative interpretation of the layered structures based on these diffractograms can not bring a valuable meaning. Detailed structural studies have been made and these results will be published in a separate paper.

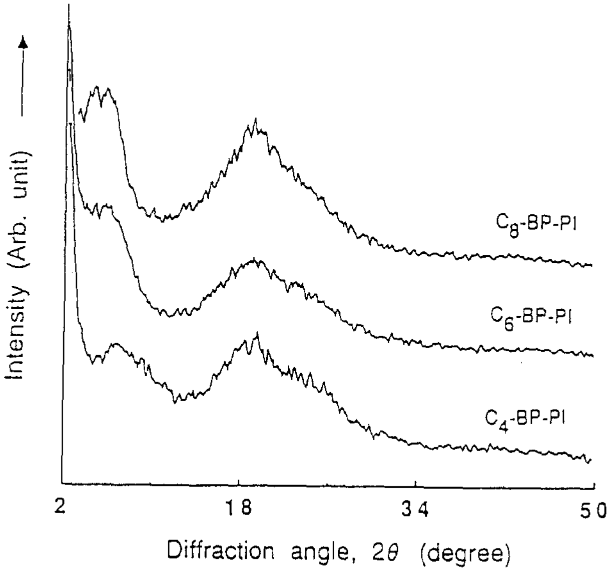


Figure 5. Wide-angle X-ray diffractograms of as-polymerized C_m-BP-PIs.

Phase transitions of C_m-BP-PIs were measured by DSC and their DSC thermograms are shown in Figure 6. In Figure 6 the upper three curves were obtained directly from as-polymerized powders and the lower three ones from C_4-, C_6- and C_8-BP-PI samples annealed at 245, 184 and 180 °C, respectively. Because upper curves are generally broad, the transitions arising from melting of side chain crystals and melting of main chain crystals are hardly identifiable. When the samples were annealed at temperatures described above, T_g's of C_4-, C_6- and C_8-BP-PIs could be measured to be 184, 135 and 127 °C, respectively, as to read from the lower curves. The decrease in T_g with increasing side chain length results from increasing plasticizing action of flexible side chain moeties toward rigid main.

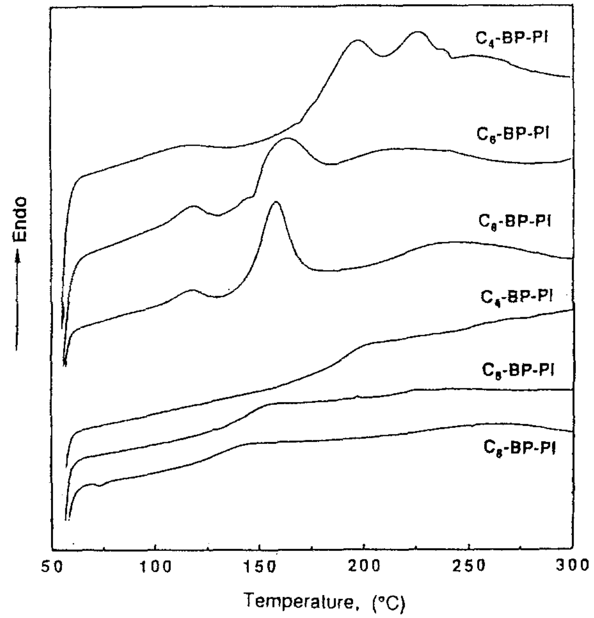


Figure 6. DSC thermograms of as-polymerized (upper curves) and annealed (lower curves) C_m-BP-PIs.

Acknowledgment

The fincial support from Korea Science and Engineering Foundation(92-48-00-01) isgratefully acknowledged.

References

1. Stenzenberger H (1976) Kautschuk, Gummi und Kunststoffe 8:477
2. Bessonov MI, Koton MM, Kudryavtsev VV, Laius LA (1987) POLYIMIDES Thermally Stable Polymers, Consultants Bureau, New York, P. 10
3. Adrova NA, Koton MM, Moskvina EM (1965) Dokl. Akad. Nauk SSSR 165:1069
4. Sroog CE (1991) Prog. Polym. Sci. 16:561
5. Ballauff M (1989) Angew. Chem. Int. Ed. Engl. 28:253
6. Ballauff M (1986) Macromolecules 19:1366
7. Helmer-Metzmann F, Rehan M, Schmitz L, Ballauff M, Wegner (1992) Makromol. Chem. 193:1847
8. Wenzel M, Ballauff M, Wegner G (1987) Makromol. Chem. 188:2865
9. Helmer-Metzmann F, Ballauff M, Schulz RC, Wegner G (1989) Makromol. Chem. 190:985
10. Park S-B, Kim H, Zin W-C, Jung JC (1993) Macromolecules 26:1627
11. Park S-B, Jung JC (1992) Makromol. Chem. 193:2519
12. Weinstock J (1961) J. Org. Chem. 26:3511
13. Jonhnston DA (1953) J. Am. Chem. Soc. 75:3636
14. Chow RC, Tarbell DS (1967) J. Org. Chem. 32:2188
15. Jung JC, Park S-B J. Polym. Sci. Part A: Polym. Chem. submitted