Polycondensation Between *p*-Dibromobenzene and *m*-Dibromobenzene

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ABSTRACT: $NiCl_2$ (bpy)-catalyzed polycondensation between *p*-dibromobenzene and *m*-dibromobenzene was carried out under various conditions. With the polycondensation, a series of copolymers with number-average molecular weights of 2400 (by gel permeation chromatography with polystyrene standards) was formed, and some samples had good solubility in organic solvents. The IR spectra and the ultraviolet spectra measured in a tetrahydrofuran (THF) solution of the copolymer showed that there were *p*-phenylene and *m*-phenylene units in the copolymer. According to analyses with differential scanning calorimetry, thermogravimetric analysis, and X-rays, with an increasing molar ratio of *m*-phenyl units in the copolymer, the glass-transition temperature, the temperature of viscous flow, and the crystallizability of the polyphenylene copolymer decreased. The fluorescence spectra of the copolymer measured in a THF solution showed an emission maximum at 373–376 nm, whereas the maximum shifted to 436.6 nm for the film. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2210–2215, 2003

Key words: polycondensation; copolymerization; conducting polymer

INTRODUCTION

In the field of conjugated polymers, polyphenylene continues to receive considerable attention because of its outstanding physical and chemical performance.[1] It is known for its exceptional thermal stability in the neutral state, good chemical stability, very wide conductive range, and optical properties. However, a major problem in the application of PPP is its insolubility in most organic solvents. The most important approach to PPP is the synthesis of soluble polyphenylene.[2]

To modify its solubility in an organic solvent, a long-chain PPP derivative has been synthesized. However, the steric demand of the alkyl chain led to a considerable torsion on the phenyl–phenyl bonds, which seriously inhibited the conjugative interaction along the polymer chain.

More recent approaches have been tried to avoid this problem. A novel and particularly promising approach toward the planarization of the PPP backbone is its incorporation into a ladder-type structure.[3,4]

In this article, the synthesis of polyphenylene copolymer, which was based on polycondensation between *p*-dibromobenzene and *m*-dibromobenzene with Yamamoto reaction,[5] is described.

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EXPERIMENTAL

Copolymerization

When 25 mg of $NiCl_2$ (bpy) was added to a mixture of the products obtained by the reaction of 5.9 g (25 mmol) of a mixture of *p*-dibromobenzene and *m*-dibromobenzene with 0.61 g (25 mmol) of magnesium in dry tetrahydrofuran (THF; 30 mL), the copolymerization was started. The copolymerization was completed after refluxing for 4 to 48 h. The reaction mixture was poured into 200 mL of methanol. The copolymer was precipitated and collected over a glass filter, washed with diluted hydrochloric acid, distilled with water and methanol, respectively, and then dried in a vacuum to yield a light yellow or white copolymer. The yield of the samples were calculated on the basis of the amount of carbon taken into the copolymer.

To remove the bromine end groups, 0.2 g of soluble copolymer was dissolved in THF (20 mL) and added dropwise to a suspension of lithium aluminum hydride (1.00 g, 26.32 mmol) in THF (20 mL) under a nitrogen atmosphere at room temperature. The reaction mixture was then refluxed for 24 h. After it was to room temperature, the reaction mixture was quenched with a $2N$ aqueous solution of H_2SO_4. The copolymer was collected over a glass filter and washed with distilled water and methanol. Then, the copolymer was dissolved in 10 mL of THF, and the solution was poured into 200 mL of methanol. The precipitated copolymer was collected over a glass filter and dried in a vacuum at room temperature.

TABLE I
Influence of the Molar Ratio of the Monomer on Polycondensation
and the Elemental Analysis Data of the Copolymer[a]

Run	Molar ratio of monomers[b]	Yield (%)	Calcd.		Found		
			H	C	H	C	Br
101	100 : 0	97.26	5.26	94.74	5.14	85.73	7.66
102	0 : 100	48.77	5.26	94.74	5.41	87.88	6.34
103	80 : 20	84.82	5.26	94.74	4.60	83.33	10.04
104	60 : 40	75.85	5.26	94.74	4.99	84.50	8.39
105	50 : 50	64.41	5.26	94.74	4.81	84.52	7.93
106	40 : 30	60.74	5.26	94.74	4.99	86.48	3.90
107	20 : 10	39.31	5.26	94.74	4.94	85.50	8.33

[a] Reaction time = 4 h, reaction temperature = 70°C, solvent = THF.
[b] *p*-Dibromobenzene/*m*-dibromobenzene.

Characterization

IR spectra of the copolymer were recorded on a Jusco IR-810 spectrometer. Ultraviolet (UV) spectra were taken with a Shimadzu UV-3100 PC scanning spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a Shimadzu DSC-50 differential scanning calorimeter and a TG-50 thermogravimetric analyzer, respectively. X-ray diffraction patterns were obtained with a Philips PC-APD X-ray diffractometer. Molecular weight and molecular-weight distribution of the copolymer were measured with a Toso HLC-8020 GPC, and the detector was a Toso UV-8020. Fluorescence spectra were obtained with a Hitachi F-4010 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

Polycondensation

The influence of the molar ratio of monomer on the polycondensation ability is shown in Table I. It suggests that we can get polyphenylene copolymer composed of *p*-phenyl and *m*-phenyl units. However, as shown in Table I, with increasing molar ratio of *m*-dibromobenzene in the monomers, the yield of product decreased. It is difficult to synthesize polyphenylene with a high degree of polymerization because of its precipitating polycondensation in most organic solvents. However, when the molar ratio between *p*-dibromobenzene and *m*-dibromobenzene in the reactive mixtures was in the range *p* monomer : *m* monomer = 3–1 : 7–9, the reaction became a solution polycondensation one, and the formed copolymer was soluble in most organic solvents, such as THF, dimethyl sulfoxide, dimethylformamide.

TGA and DSC of the copolymer

Polyphenylene, consisting of coupled aromatic nuclei, has a high heat-resistance performance. Figures 1 and 2 show the TGA and DSC spectra of PPP, polymetaphenylene (PMP), and the polyphenylene copolymer separately. As shown in the DSC spectra, the glass-transition temperature (T_g) of PPP was over its T_d, and the T_g of PMP was 104.9°C. As shown in Table II, with the increase of *p*-phenylene units in the copolymer, the T_g of the copolymer increased, and all of the copolymers had thermal stabilities higher than did PMP. When the molar ratio of the reaction mixture was in
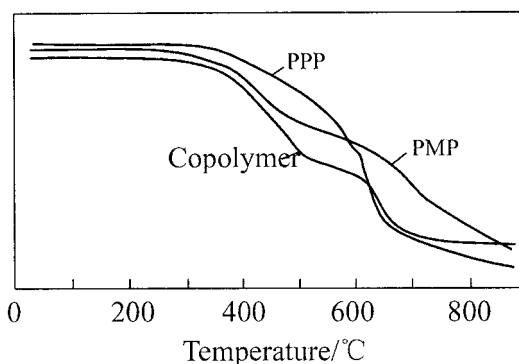

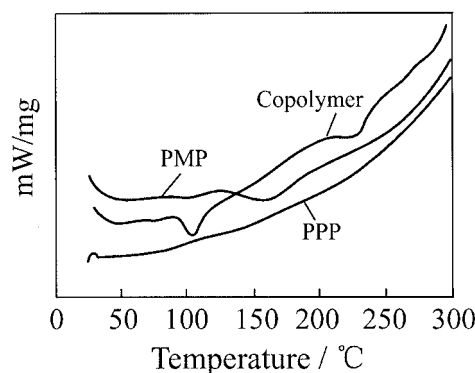**Figure 1** TGA spectra of PPP, PMP, and the polyphenylene copolymer.

Figure 2 DSC spectra of PPP, PMP, and the polyphenylene copolymer.

TABLE II
Influence of *m*-Phenyl Units of the Copolymer
on its T_g, T_f, and T_d

m units/*p* units	T_g (°C)	T_f (°C)	T_d (−5%, °C)
100/0	104.93	227.62	360
80/20	105.30	131.48	400
60/40	130.17	166.02	425
50/50	153.18	>300	390
40/60	162.94	>300	400
20/80	>300	>300	420
0/100	>300	>300	375

TGA conditions: nitrogen atmosphere, heating speed = 10°C/min. DSC conditions: helium atmosphere, heating speed = 10°C/min.

the range 4–1 : 6–9 (*p*-dibromobenzene *m*-dibromobenzene), formed copolymer became thermoplastic material.

IR and NMR analyses of the copolymer

Figure 3 shows the IR spectra of PPP [Fig. 3(a)], PMP [Fig. 3(c)], the copolymer [Fig. 3(b)], and the bromine-removed copolymer [Fig. 3(d)].[5–9] If PPP has a strictly linear structure, it should display an IR spectra without absorption at 850–900 and 1590–1600 cm^{-1} and should have a single weak absorption at 900 cm^{-1}. The band at 808 cm^{-1} was the out-of-plane vibration of *p*-phenylene units, and the peak 1475 cm^{-1} was the absorption bands of 1,4-substituted benzene ring. However, there are an absorption band at 1594 cm^{-1} ($\nu_{c=c}$) for PMP. As shown in Figure 1, we found characteristic absorption bands of *p*-phenylene units (1471 and 812 cm^{-1}) and characteristic bands of *m*-phenylene units (1594 and 775 cm^{-1}) in the copolymer.
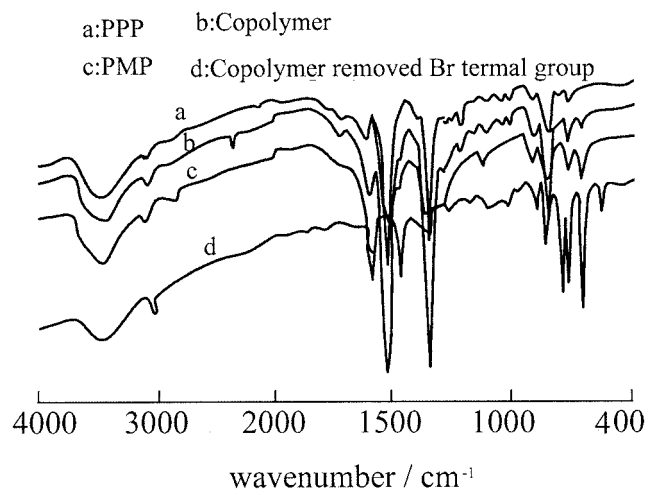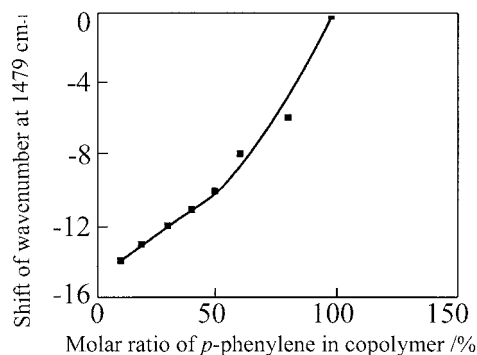

Figure 4 Influence of the molar ratio of *m*-phenylene units on the IR spectra.

It was very interesting that the bathochromic shift of the 1475 cm^{-1} adsorption band in the copolymer had actually taken place. Figure 4 shows the influence of the molar ratio of the *m*-phenyl units on the bathochromic shift of the 1475 cm^{-1} absorption band. With increasing molar ratio of the *m*-phenylene units in the copolymer, the absorption of the *p*-phenylene units observed at 1475 cm^{-1} shifted to a low wavenumber.

There were some terminal bromine groups in the copolymer synthesized by the Yamamoto method. To remove the bromine end groups, the THF solution of the copolymer was hydrogenated by lithium aluminum hydride. As shown in Figure 3(b), 761 cm^{-1} was the absorption band of the *p*-bromophenyl group. However, in Figure 3(d), the absorption band disappeared. We suggest that the terminal bromine groups were substituted by hydrogen. The results of elemental analysis showed that there were no bromine atoms in the hydrogenated copolymer.

Figure 5 shows the ^{1}H-NMR spectra of the soluble polyphenylene copolymer. In the copolymer, a very strong single peak at $\delta = 7.649–7.654$ and a very weak single peak at $\delta − 7.870$ [Fig. 5(a)] or $\delta − 7.856$ [Fig.
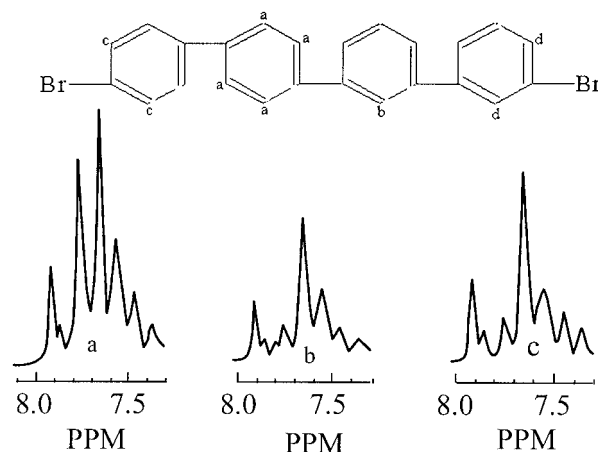

Figure 3 IR spectra of PPP, PMP, and polyphenylene copolymer.

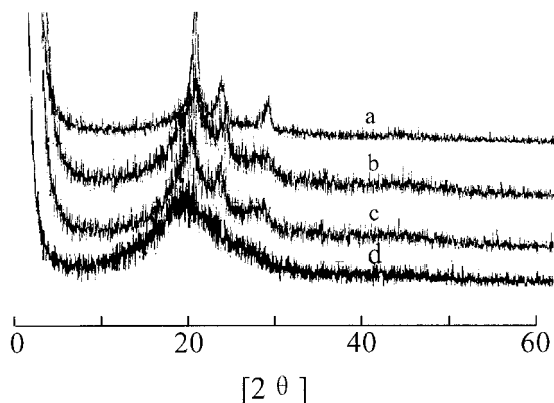**Figure 5** ^{1}H-NMR spectra of the polyphenylene copolymer.

Figure 6 X-ray diffraction analysis of the copolymer.

5(b)] were observed, characterizing protons a and b, respectively. Proton c was characterized with a weak single peak at $\delta - 7.558$ [for Fig. 5(b)]. When the terminal bromine group in the copolymer was substituted, the peak disappeared as shown in Figure 5(c).

TABLE III
UV Absorption Maxima of *p*-Phenyl Units
of the Copolymer Solution in THF

Run	*p* units/*m* units (molar ratio %)	λ_{max} (nm)	Average of repeatedly linked *p*-phenylene units
01	80/20	300.8	4.10
02	50/50	293.2	3.60
03	40/30	289.4	3.4
04	30/70	257.6	2.22
05	20/80	255.4	2.15
06	10/90	253.2	2.09

X-ray diffraction patterns of the copolymer

Figure 6 shows X-ray diffraction patterns of the powdery polymer. The X-ray diffraction patterns of the polymer showed that the PPP had a high crystallinity, but PMP was an amorphous polymer. With increasing *m*-phenylene units in the copolymer, the crystallinity of the copolymer decreased, whereas the solubility in organic solvents increased.

UV absorption and fluorescence properties of the polymers

The UV–visible spectra of the copolymer depended markedly on the molar ratio of *p*-phenylene units in the copolymer. According to UV analysis, the absorption maximum (λ_{max}) appeared at 251.8 nm for PMP. When *m*-phenylene units in the polymer were present, conjugation along the chain backbone was prohibited. With increasing molar ratio of *m*-phenylene units in the materials, the number of repeatedly linked *p*-phenylene units decreased, and λ_{max} blue shifted. With λ_{max} of *p*-phenylene groups in the copolymer, the average of repeatedly linked *p*-phenylene units in the copolymer was calculated, and the results are shown in Table III.

Figure 7 shows the fluorescence spectra of diluted solutions of PPP, PMP, and the polyphenylene copolymer in THF. Figure 7(a) is the fluorescence spectra of PPP. As shown in Figure 7(a), there were two peaks in the excitation spectra of PPP at 246.2 nm (peak a) and 306.2 nm (peak b) separately. The intensity of peak a was lower than peak b (curve a). Curve b ($\lambda_{max} = 304.8$ nm) is the emission spectrum for the excitation wavelength at 246 nm, and Curve c ($\lambda_{max} = 372.6$ nm) is the
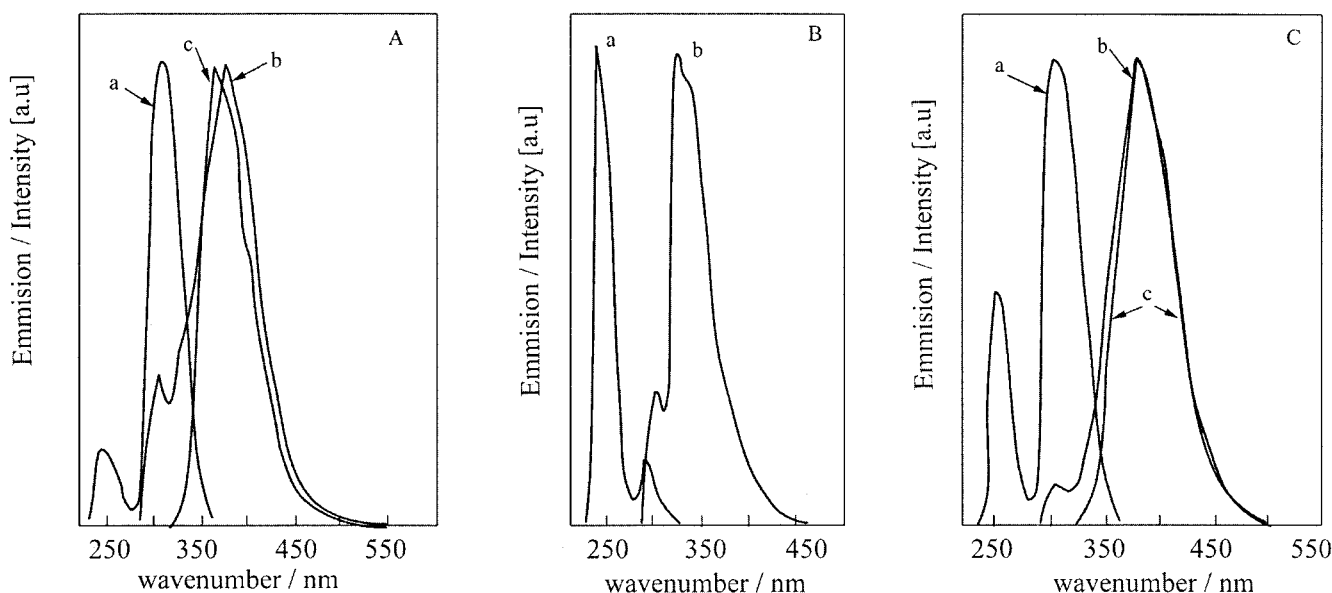

Figure 7 Fluorescence spectra of PPP, PMP, and the polyphenylene copolymer solution in THF.

TABLE IV
Data of the Fluorescence Spectra of PPP, PMP, and Copolymer

Polymer (p units/m units)	Excitation spectrum		Emission spectrum	
	$\lambda_{\text{max}_{\text{peak}}}{}^{\text{I}}$ (nm)/ intensity (au)	$\lambda_{\text{max}_{\text{peak}}}{}^{\text{II}}$ (nm)/ intensity (au)	$\lambda_{\text{max}_{\text{peak}}}{}^{\text{I}}$ (nm)/ intensity (au)	$\lambda_{\text{max}_{\text{peak}}}{}^{\text{II}}$ (nm)/ intensity (au)
100 : 0	246.2/128.6	306.2/775.1	304.8/42.31	372.6/768.9
0 : 100	247.2/217.0	291.4/32.59	306.0/332.2	
80 : 20	244.0/111.1	318.4/640.6	376.0/111.3	377.4/638.0
60 : 40	244.0/121.1	317.6/442.7	373.8/121.8	376.2/447.9
50 : 50	248.0/380.3	302.4/741.0	375.6/383.0	376.0/745.3
40 : 60	248.0/429.1	301.4/669.6	374.6/426.7	376.6/665.2
20 : 80	248.0/273.1	296.8/213.7	353.2/275.1	355.8/219.4
			369.2/240.1	371.8/228.5

The concentration of the copolymer solution in THF was controlled in the range 0.1–0.3%.

emission spectra for the excitation wavelength at 306 nm. Figure 7(b) is the fluorescence spectra of PMP. As shown in Figure 7(b), there were two peaks in the excitation spectra of PMP at 247.2 nm (peak a) and at 291.4 nm (peak b), separately too. However, the intensity of peak b was lower than that of peak a (curve a). Curve b (λ_{max} = 306 nm) is the emission spectrum for the excitation wavelength at 247 nm.

Figure 7(c) is the fluorescence spectra of the polyphenylene copolymer (p/m = 5 : 5). As shown in Figure 7(c), there were two peaks in the excitation spectra of the copolymer at 248 nm (peak a) and 302.4 nm (peak b) separately. The intensity of peak a was smaller than peak b (curve a). Curve b (λ_{max} = 375.6 nm) is the emission spectra for the excitation wavelength at 248 nm, and curve c (λ_{max} = 376.0 nm) is the emission spectra for the excitation wavelength at 302 nm. The data of intensity for the fluorescence spectra of PPP, PMP, and the copolymer were collected in Table IV. Fluorescence analysis of copolymer, with the removed terminal bromine group, showed bromine group in copolymer did not influence on the fluorescence spectra of copolymer.
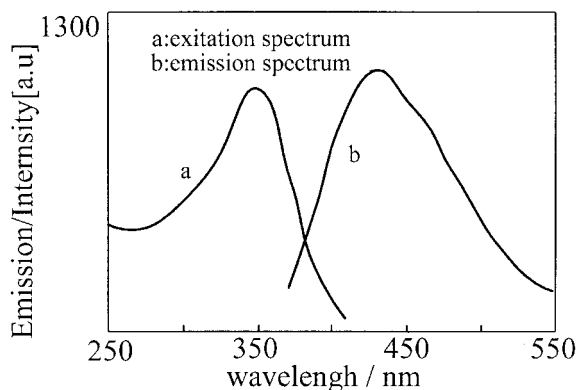
As shown in Table IV, to stimulate an electron to excitation, the energy needed for PMP was higher than that needed for PPP ($\lambda_{\text{max}_{\text{PMP}}} < \lambda_{\text{max}_{\text{PPP}}}$), but the maximum intensity of the emission spectra of PPP was higher than that of PMP. We suggest that the intensity of stimulated fluorescence decreased with the increasing m-phenylene units in the copolymer because of poorer conjugation along the chain backbone of the copolymer.

Figure 8 shows the fluorescence spectra of the copolymer measured with a thin film cast on a quartz plate. The intensity data of the fluorescence emission spectra for the copolymer with different molar concentrations of p-phenylene units are shown in Table V. Here, a bathochromic shift of nearly 34–64 nm for the copolymer was observed.

CONCLUSIONS

Polyphenylene copolymer composed of p-phenylene and m-phenylene was synthesized with dehalogenation between p-dibromobenzene and m-dibromobenzene, promoted by $NiCl_2$ (bpy). The copolymer had a good thermal stability and optical properties. With the increase of m-phenylene unit content in the copolymer, the T_g, temperature of viscous flow (T_f), and crystallinity of copolymer decreased. When the molar ratio of m-phenylene units in the copolymer was more

Figure 8 Fluorescence spectra of the polyphenylene copolymer film on a quartz plate.

TABLE V
Fluorescence Data of the Copolymer

Molar ratio of p units and m units in the copolymer (p units/m units)	Excitation spectrum		Emission spectrum	
	λ_{max} (nm)	Intensity (au)	λ_{max} (nm)	Intensity (au)
30 : 70	369.2	1174	436.6	1164
20 : 80	348.6	983.8	431.8	1064
10 : 90	341.4	420.5	405.2	385

than 70%, the copolymer had excellent solubility in most organic solvents and excellent film-forming properties.

References

1. Lacaze, P. C.; Aeiyach, S.; Lacroix, J. C. In Handbook of Organic Conductive Molecules and Polymers. Vol. 2. Conductive Polymer: Synthesis and Electrical Properties: Nalwa, H. S., Ed.; Chichester, England: Wiley, 1997; p 205.
2. Yamamoto, T.; Wu, B. Y.; Choi, B.-K.; Kubota, K. Chem Lett 2000, 720.
3. Scherf, U.; Bohnen, A.; Mullen, K. Makromol Chem 1992, 193, 1127.
4. Kreyenschmidt, M.; Ucket, F.; Mullen, K. Macromolecules 1995, 28, 4577.
5. Yamamoto, T.; Hayashi, Y.; Yamamoto, A. Bull Chem Soc Jpn 1978, 51, 2091.
6. Aeiyach, S.; Lacaze, P. C. J Chim Phys Chim Biol 1989, 86, 143.
7. Socrates, G. Infrared Characteristic Group Frequencies; Chichester, England: Wiley, 1980.
8. Murray, D. P.; Dechter, J. J.; Kispert, L. D. J Polym Sci: Polym Lett Ed 1984, 22, 519.
9. Tieke, B.; Bubeck, C.; Lieser, G. Makromol Chem Rapid Commun 1982, 3, 261.