

Copolymerization of bis(chlorophthalimide)s with 2,5-dichlorobenzophenone catalyzed by NiBr₂/PPh₃/Zn

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Received 15 April 2005; received in revised form 13 June 2005; accepted 5 July 2005

Abstract

Copoly(phenylene-imide)s were synthesized by Ni(0)-catalyzed coupling of aromatic dichlorides containing imide structure and 2,5-dichlorobenzophenone. The route offered the flexibility of incorporating different ratios of benzophenone and imide groups in the polymer backbone in a controlled manner. The resulting copolymers exhibited high molecular weights (high inherent viscosity), and a combination of desirable properties such as good solubility in dipolar aprotic solvents and cresols, film-forming capability and good mechanical properties. Wide-angle X-ray diffractograms revealed that the polymers were amorphous. These copolymers had glass transition temperatures between 209 and 319 °C and 10% weight loss temperatures in the range of 502–543 °C in nitrogen atmosphere. The tough polymer films, obtained by casting from *N*-methylpyrrolidone solution, had a tensile strength range of 83–156 MPa and a tensile modulus range of 1.6–3.6 GPa.
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Keywords: Poly(phenylene-imide)s; Ni(0)-catalyzed coupling copolymerization; High solubility

1. Introduction

Aromatic polyimides are certainly one of the most successful classes of high-performance polymers and are widely used in many applications such as electrics, coatings, composite materials and membranes [1,2]. Because of the rigidity of the imide ring, most polyimides possess high thermal resistance, high tensile strength and high modulus. However, the commercial use of these materials is often limited because of their poor solubility and high softening or melting temperatures. Thus, one of the targets of polyimides chemistry is to incorporate new functionalities to improve their solubility without decreasing the above properties. For this purpose, chemical modifications of their structure have been made by incorporating bulky side groups [3–7], flexible spacers [8–12], kinked [13,14] or unsymmetrical structures [15–18] into the polymer backbone.

Copolymerization is another popular synthetic approach to obtain processable and soluble polyimides [19,20].

Specific monomers, containing the desired functionalities, are required for the copolymer synthesis. Bis(chlorophthalimide)s monomers have been easily synthesized from chlorophthalic anhydride and diamines. With these monomers, biphenyl types of polyimides have been prepared by the nickel catalytic coupling polymerization [21]. Its copolymerization with dichlorodiphenylsulfone has also been investigated by us [22].

The monomer 2,5-dichlorobenzophenone is potentially inexpensive because it can be synthesized from 1,4-dichlorobenzene and benzoyl chloride. With this monomer, poly(2,5-benzophenone), a polymer first disclosed by chemists at Maxdem Inc. [23], was synthesized by nickel catalytic coupling polymerization and this coupling reaction was developed and detailed by Quirk [24], Sheares [25] and McGrath [26]. This poly(*p*-phenylene) polymer displayed good solubility in dipolar aprotic solvents, and excellent thermal and mechanical properties. However, poly(2,5-benzophenone), in general, formed very brittle films [27–29]. The inability to forming flexible films limited its application, such as gas separation membranes, low dielectric constant materials, etc.

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In this article, we report the copolymerization of 2,5-dichlorobenzophenone with bis(chlorophthalimide)s by nickel catalytic coupling polymerization. We expect that the combination polyimide and other high-performance macromonomers will allow one to produce new materials that represent a balance of homopolymer properties.

2. Experimental

2.1. Materials

Reagent grade anhydrous NiBr₂ was dried at 220 °C under vacuum. Triphenylphosphine (PPh₃) was recrystallized from hexane. Powdered zinc was stirred with acetic acid, filtrated, washed thoroughly with ethyl ether, and dried under vacuum. 4-Chlorophthalic anhydride (99.2%) was purified by distillation. 4,4'-Oxydianiline (ODA), 3,3'-dimethyl-4,4'-methylenedianiline (DMMDA), 4,4'-methylenedianiline(MDA), 4,4'-(9-fluorenylidene)dianiline (FDA), 1,4-dichlorobenzene and benzoyl chloride were used as received from Aldrich. *N,N*-Dimethylacetamide (DMAc) and *N*-methylpyrrolidone (NMP) were dried over CaH₂, distilled under reduced pressure, stored over 4 Å molecular sieves.

2.2. Characterization

The ¹H NMR spectrum and ¹³C NMR spectra were measured at 600 MHz on an AV600 spectrometer. FT-IR spectra were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer. The elemental analyses were performed on an elemental analysis FLASH-EA-1112-Series. The inherent viscosities were determined at a 0.5% concentration of polymer in *m*-cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer and the experiments were carried out with 10 ± 2 mg samples at a heating rate of 10 °C/min. The dynamic mechanical properties of PI films were measured on a dynamic mechanical thermal analyzer (DMTA-δ). The mechanical properties of the films were measured on a mechanical tester Instron-1211. The wide angle X-ray diffraction (WXR) measurements were undertaken on a Philos X-ray diffractometer with Cu K_α radiation (40 kV, 30 mA). The scanning rate was 2 °/min. UV-visible absorption spectra were obtained on a SHIMADZU UV-2550 spectrometer with 1.0 cm quartz cells.

2.3. Monomers synthesis

Bis(4-chlorophthalimide)s **1a–1d** were prepared from 4-chlorophthalic anhydride and diamines **a–d**, respectively, using the same procedure as described in literature [21].

2.3.1. 4,4'-Bis(4-chlorophthalimido)diphenylmethane (**1c**)

The compound was white powder (yield 81%). mp 258–260 °C. ¹H NMR (CDCl₃) δ = 7.95 (d), 7.94 (s), 7.91 (s), 7.80 (d), 7.77 (d), 7.39 (m), 7.29 (s), 4.13 (s). FT-IR: 1773 and 1721 cm⁻¹ (ν_{C=O} of imide), 1375 cm⁻¹ (ν_{C-N}). Anal. Calcd for C₂₉H₁₆Cl₂N₂O₄: C, 66.05%; H, 3.06%; N, 5.31%. Found: C, 66.01%; H, 3.12%; N, 5.31%.

2.3.2. 2,5-Dichlorobenzophenone (**2**)

The compound was directly synthesized by anhydrous aluminum chloride-catalyzed, Friedel–Crafts acylation of 1,4-dichlorobenzene with benzoyl chloride. The yield was 62%. mp 90–91 °C (lit. [27] 93 °C).

2.4. Polymers synthesis

A 100 mL three-necked round-bottomed flask equipped with serum caps, nitrogen inlet and outlet was placed with anhydrous NiBr₂, PPh₃ and zinc dust. The flask was evacuated and filled with nitrogen three times. Then dried DMAc was added via syringe through the serum caps. The mixture was stirred at 80 °C. When the mixture changed into red-brown after 30 min, a nitrogen purged solution of two monomers in dry DMAc was added via syringe to the mixture. The mixture was stirred at 80 °C for another 2–4 h. The resulting viscous mixture was poured into 300 mL of 25% HCl/methanol. The solid was collected and washed with methanol and water, then dried in vacuum oven at 200 °C for 10 h.

2.5. Films preparation

Polymer films were prepared by casting 8 wt% solutions of polymers in NMP on glass plates in a dust-free room, and dried at 70 °C overnight, then at 200 °C for 48 h in vacuum oven.

3. Results and discussion

3.1. Monomer synthesis

1a–1d were prepared as described in the literature [21], and treated above 200 °C to ensure imidization completely, then recrystallized to ensure the purity above 99%. High purity of monomers is very important for Ni(0)-catalyzed polymerization due to low purity can lead to low molecular weight.

3.2. Polymer synthesis and characterization

The Nickel(0)-catalyzed copolymerization was performed with 2 mmol of 2,5-dichlorobenzophenone and 2 mmol of bis(4-chlorophthalimide)s in DMAc in presence of anhydrous NiBr₂, zinc dust and triphenylphosphine. The effects of temperature, solvent volume and the amount of

nickel catalyst on molecular weight were studied by following the copolymerization of monomer **1b** and **2**. The optimal amount of solvent for 1 mmol scale reaction was 4–6 mL. This volume of solvent provided the necessary solubility and mobility of the reaction system and led to reasonable reaction time. The highest inherent viscosity was observed with a 14 mol% concentration of nickel catalyst. An increase in nickel catalyst led to the formation of long-lived nickel species at polymer ends which would lead to lower molecular weight materials [21]. The copolymerization was performed at 80 °C. Raising the temperature to above 100 °C gave inferior results because higher temperature would favor the formation of the highly coordinated bis complex $[\text{Ni}(\text{PPh}_3)_2]$, and then the oxidative addition of triphenylphosphine could occur [23].

A series of copolymers were synthesized by the Nickel(0)-catalyzed coupling copolymerization of bis(4-chlorophthalimide)s with 2,5-dichlorobenzophenone (Scheme 1). The copolymer products were isolated by precipitation in HCl/methanol and purified by resolving in DMAc and precipitated in methanol alternately for several times. The results of the polymerizations were listed in Table 1. The formations of copolymers were confirmed by elemental analysis and FT-IR spectroscopy. In this copolymerization, 4-chlorophthalimides had a wide selective range of diamine structure and the products had high molecular weight, yet most of the homopolymers of **1** were oligomers [21]. This phenomenon suggested that the introduction of 2,5-dichlorobenzophenone which contained bulky lateral group could give products with high molecular weight.

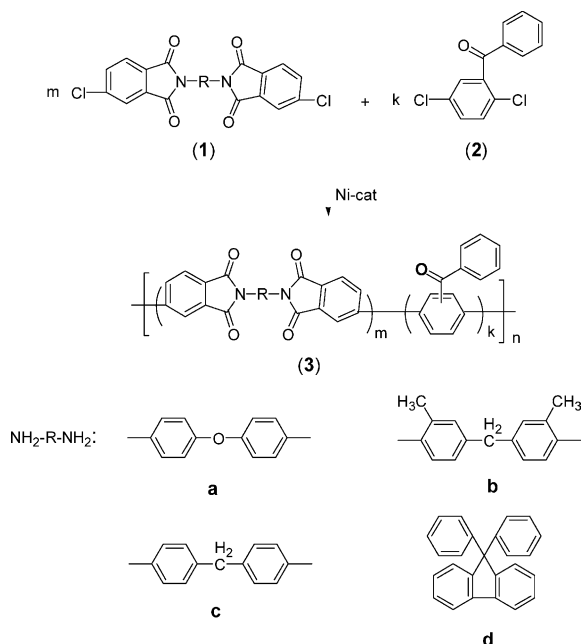
Further work has been carried out to investigate the polymerization capability. The copolymers with different

mole ratios of the **1b** to **2** denoted as **3b-x** were obtained, where *x* was the mole fraction of **2** in the feed. The results of the polymerizations were also listed in Table 1. The formations of copolymers **3b-x** were confirmed with elemental analysis (Table 1), FT-IR spectroscopy (Fig. 1), and ultraviolet–visible absorption spectroscopy (Fig. 2). The results of elemental analysis supported the formation of the expected polymers. As shown in Fig. 1, the FT-IR spectra of **3b-x** exhibited characteristic absorption bands of imide group at 1775 and 1725 cm^{-1} ($\nu_{\text{C=O}}$), 1370 cm^{-1} ($\nu_{\text{C-N}}$) and 743 cm^{-1} (C=O bending). The absorption band at 1660 cm^{-1} could be assigned to C=O stretching vibration of carbonyl group in benzophenone units, and its intensity increased as the amount of **2** increased.

The UV–vis absorption spectra of **3b-x** were shown in Fig. 2. The absorption maximum of homopolymer of **1b** and **2** were at 263 and 327 nm (328 nm reported in lit. [24]), respectively. The absorption maximum moved to longer wavelength with the amount of **2** increasing indicated that the structure of the copolymers were more conjugated. It was also suggested that **1b** and **2** were perfectly combined. Wide-angle X-ray diffraction (WAXD) investigation of these polymers provided broad curves of amorphous structures.

Previously, the Sheares group had reported [27–29] that polymerization of 2,5-dichlorobenzophenone via Ni(0)-catalyzed coupling in amide solvents led to partial reduction of carbonyl functionalities to the secondary alcohol, which had a drastic influence on the polymer physical properties. The resulting polymer contained signals at about 80.0 ppm in ^{13}C NMR spectrum which were identified as the secondary alcohol group. Broad and strong absorption band at about 3500 cm^{-1} was assigned to –OH absorption band in FT-IR spectra [29].

Copolymerizations of bis(chlorophthalimide)s and **2** in this work were all carried out in DMAc. THF was found to be unsuitable solvent for this copolymerization, due to the poor solubility of the resulting polymers in THF. The ^1H NMR and ^{13}C NMR spectra of polymer **3b** were shown in



Scheme 1. Syntheses of copolymers **3a–3d**.

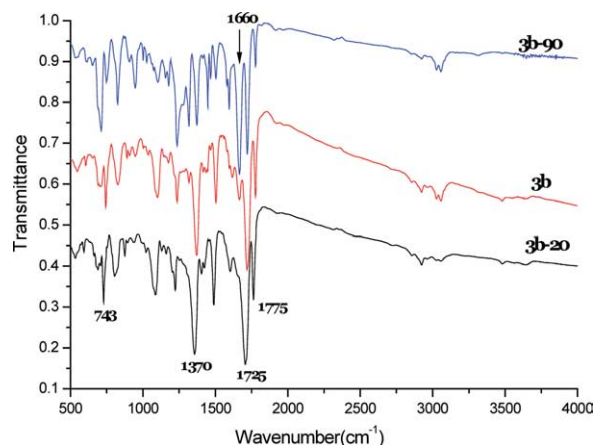


Fig. 1. FT-IR spectra of **3b** and **3b-x**.

Table 1
Preparations of polymers

Samples	Reaction time (h)	Yield (%)	η_{inh} (dL/g)	Elemental analysis			
				C		N	
				Calcd	Found	Calcd	Found
3a	3	96	0.54	77.12	77.01	4.39	4.30
3b	3	100	0.87	79.52	79.31	4.21	4.20
3c	4	95	0.45	79.25	79.27	4.40	4.32
3d	4	100	0.68	82.44	82.35	3.56	3.62
3b-20	4	100	0.81	77.69	77.71	5.29	5.18
3b-90	4	100	0.95	84.41	84.29	1.33	1.45

Figs. 3 and 4. The peaks appeared at 4.1 and 2.1–2.2 ppm (Fig. 3) were assigned to $-\text{CH}_2-$ and $-\text{CH}_3$ of phthalimide units in **3b**. No characteristic signal of the secondary alcohol was found in ^{13}C NMR spectrum. In addition, the FT-IR spectra of **3b** and **3b-x** (Fig. 1) also showed no a broad and strong $-\text{OH}$ absorption band at about 3500 cm^{-1} . The three spectra gave good proofs that no reduction of carbonyl functionalities could be observed in copolymerization.

Three main possible link types in **3b** when the two monomers combined were shown in Scheme 2. The chemical shifts of C_1 and C_2 were at 146.5 ppm in Fig. 4 which was in agreement with the results of literature [30]. The chemical shifts of C_5 and C_8 were at 168.4 ppm [30], 198.0–200.0 ppm [24], respectively. The proportion of the integral value of C_5 to C_8 is about 4:1 which showed that the two monomers were coupled together quantitatively. Compared with the spectra of homopolymers showed in Fig. 5, several new signals of tertiary carbon appeared in spectrum of **3b** (labeled with star). New broad signals I and II appeared in low field should be assigned to C_3 and C_4 which connected with structure **B**. The different length of

structure **B** led to broad peaks. While the chemical shift of C_7 moved to up field to give the new signal IV. The other two new signals III and V should be assigned to C_{10} and C_9 , respectively. The proportion of the integral value of C_1 and C_2 to the total of new signals III and V was about 1:1 which indicated that in the polymer **3b** the proportion of homo-coupled structure (**A** and **B**) to the cross-coupled structure (**C**) was about half to half. Yet we could not determine the exact structure and the length of the cross-coupled section.

As shown in Table 2, glass transition temperatures (T_g) of the copolymers changed between $319\text{ }^\circ\text{C}$ (**3b-20**) and $209\text{ }^\circ\text{C}$ (**3b-90**). For polymer **3b**, **3b-20** and **3b-90**, T_g decreased with the increase of the amount of **2**. **3b-90** exhibited a glass transition temperature of $209\text{ }^\circ\text{C}$ which was about $110\text{ }^\circ\text{C}$ lower than that of **3b-20**. This decrease was attributed to the flexible nature of the $-\text{C}=\text{O}$ group and the increase of free volume by the introduction of benzophenone moiety.

Table 2 showed the thermal stability of these amorphous copolymers investigated by thermogravimetric analysis (TGA). Samples of copolymers underwent weight loss from 30 to $700\text{ }^\circ\text{C}$ in nitrogen with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Thus, the copolymers displayed higher thermal oxidative stability than the corresponding homopolyimides reported in literature [21]. For polymer **3b-x**, 10% weight loss temperature increased with the increase of the amount of **2** which indicated that introduction of biphenylene structure to the polymer backbone could improve the thermal stability greatly.

One of the main objectives of this work was the improvement of the solubilities of polyimides by introducing bulky pendent groups via copolymerization while retaining thermal stability. The solubilities of copolymers were summarized in Table 3. Polymers were all soluble in phenolic solvents, and also soluble in dipolar aprotic solvents except for **3c**. Furthermore polymer **3b** and **3b-90** had good solubilities in THF. As expected, the introduction of benzophenone moiety into polyimide was effective in producing soluble polymers.

The most noticeable feature of copolymers was their ability to form transparent, flexible films. The tough polymer films, obtained by casting from NMP solution,

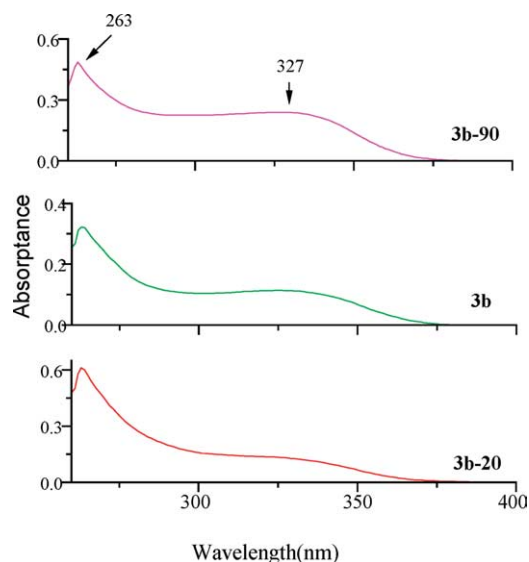
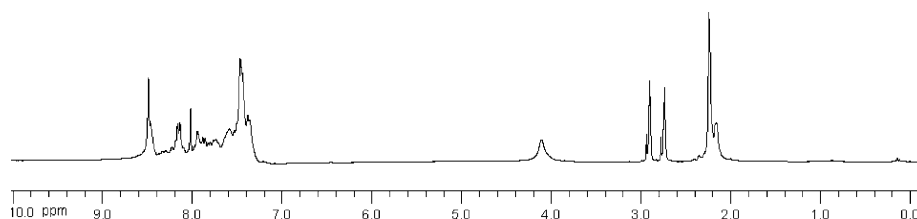


Fig. 2. Ultraviolet-visible spectra of **3b** and **3b-x**.

Fig. 3. ^1H NMR spectrum of **3b** (in $\text{DMF-}d_7$).Table 2
Thermal stabilities of polymers

Samples	T_g ($^{\circ}\text{C}$)	10% Weight loss temperature ^a ($^{\circ}\text{C}$)
3a	221	534
3b	262	526
3c	216 ^b	507
3d	252	502
3b-20	319	511
3b-90	209	543

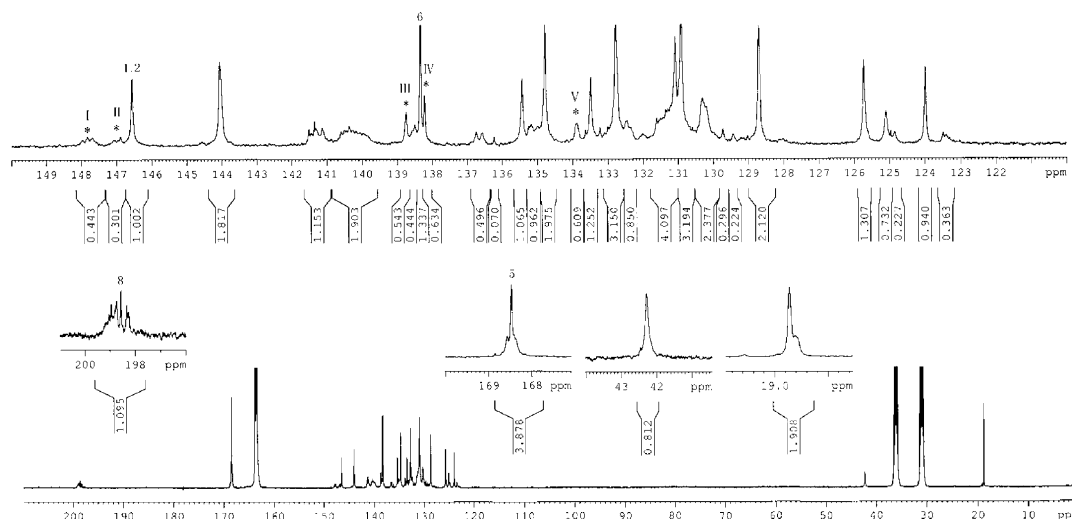
^a Determined by TGA in N_2 .^b Determined by DSC, others are all determined by DMA.Table 3
Solubility of polymers

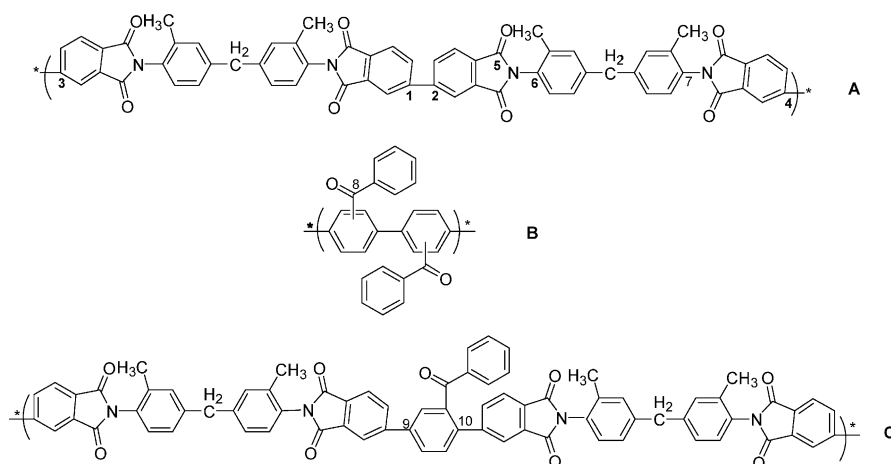
Samples	NMP	DMAc	DMF	DMSO	Cresol	THF
3a	+	+	±	±	+	–
3b	+	+	+	+	+	+
3c	+	±	±	–	+	–
3d	+	+	+	+	+	–
3b-20	+	+	+	+	+	±
3b-90	+	+	+	+	+	+

Carried out at a concentration of 10 wt% of polymer at ambient temperature, key: +, soluble; ±, swelling; –, insoluble.

exhibited good mechanical properties as displayed in Table 4 (Film **3c** cast from NMP solution was too brittle to be tested), which indicated that they were tough enough to be used as functional membrane materials. Obviously tensile strength and tensile modulus increased with

increasing the amount of **2** which indicated that the amount of benzophenone units presented in the copolymer had an effect on their mechanical properties. It is anticipated that the introduction of benzophenone units to the PIs backbone can improve some potential properties of the materials.

Fig. 4. ^{13}C NMR spectrum of **3b** (in $\text{DMF-}d_7$).

Scheme 2. Possible structures in **3b**.Table 4
Mechanical properties of polymers

Samples	Tensile strength (MPa)	Elongation (%)	Tensile modulus (GPa)
3a	97	4.2	2.5
3b	141	7.2	3.1
3d	83	5.3	1.6
3b-20	138	7.0	2.9
3b-90	156	8.8	3.6

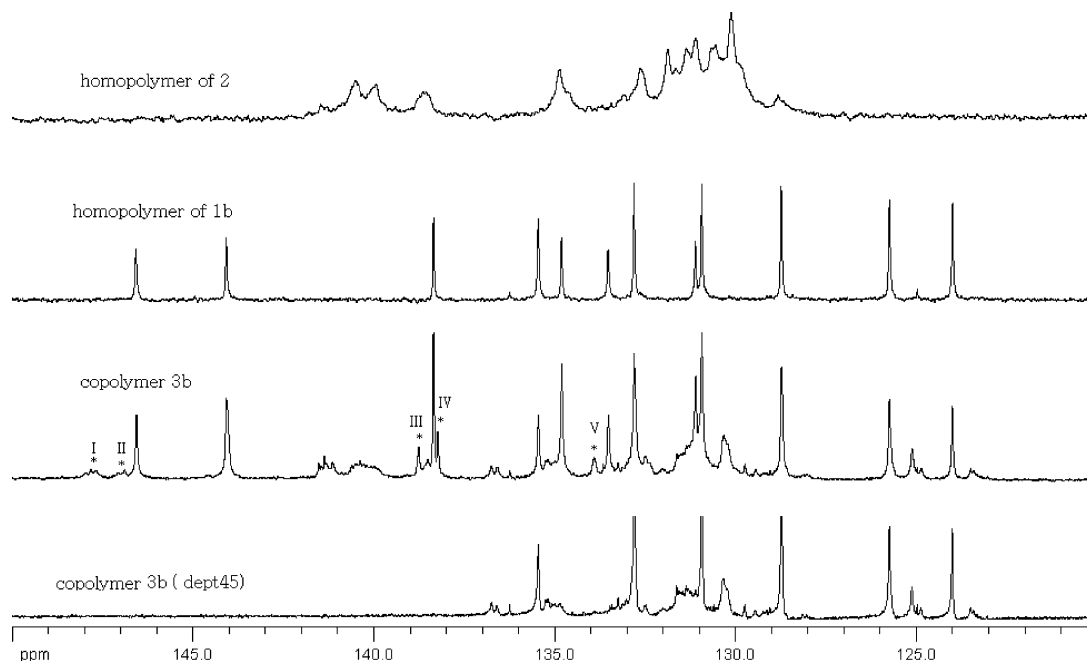
benzophenone and phthalimide structures can be copolymerized together with any mole ratios to give polymers with high inherent viscosities, and the amine structure in monomer **1** has a wide selective range. The insertion of benzophenone group into the polyimide chain can improve the properties of the polymer such as solubility, thermo-oxidative stability and mechanical property, which looks promising for the potential use as high performance material.

4. Conclusions

The results are good demonstrations for the feasibility of synthesizing polyimides containing new functional structures via Ni(0)-catalyzed coupling polymerization under mild conditions. The aromatic dichlorides containing

Acknowledgements

We thank the National Basic Research Program of China (No. 2003CB615704) and the National Science Foundation of China (No. 20474061) for the financial support.

Fig. 5. ^{13}C NMR spectra of **3b** and homopolymers of **1b** and **2** (in $\text{DMF-}d_7$).

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