

Note

POLYMERIZATION OF *p*-DIETHYNYLBENZENE
INITIATED BY $\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2(\text{PPh}_3)_2^*$

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Abstract Homogeneous polymerization of *p*-diethynylbenzene initiated by nickel acetylide $\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2(\text{PPh}_3)_2$ has been investigated in terms of different solvents, addition agents, atmosphere gases, catalyst concentrations, monomer concentrations and polymerization temperatures. The yield and catalytic efficiency approach 88% and 11.1 kg polymer/mol Ni, respectively, under the optimum conditions: $[\text{cat}] = 0.01 \text{ mol/L}$, $[\text{M}] = 1.0 \text{ mol/L}$, NEt_3/cat (mol ratio) = 3~5, 1,4-dioxane/toluene (volume ratio) = 1 and $T = 25^\circ\text{C}$ for 5 h. The polymerization rate equation can be expressed as $R_p = k_p[\text{M}][\text{cat}]^2$, where $k_p = 0.47 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ (25°C). The overall polymerization activation energy was found to be $203 \text{ kJ} \cdot \text{mol}^{-1}$. Poly(*p*-diethynylbenzene) so obtained is soluble in THF, CHCl_3 and toluene with weight-average molecular weights as high as 27, 100 and a rich-*trans* extended π -conjugated polyene chain structure with pendent groups of $p\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$.

Keywords Polymerization, *p*-Diethynylbenzene, Nickel acetylide, Catalyst

INTRODUCTION

In the past 30 years, synthesis and properties of substituted polyacetylenes have been intensively investigated. Polyacetylenes have analogous π -conjugated structures, which endow them with potential applications in photoconductivity, optical nonlinear susceptibility and magnetic susceptibility^[1]. Poly(*p*-diethynylbenzene), PDEB, is a member of the polyacetylene family. Some patents reported its potential applications in electronics and optics^[2-4]. Recently, we found that soluble PDEB shows conductivity^[5, 6], electroluminescence^[7, 8], third-order nonlinear optical property^[9] and humidity sensitivity^[10, 11]. However, PDEB prepared by other methods, such as thermal^[12], high pressure and sheer^[13], irradiation^[14], electroinitiated^[15] and catalytic polymerization methods^[16, 17], is insoluble in organic solvents, unstable in air and of low molecular weight ($< 15,000$).

In recent years, transition metal acetylides were found to be effective catalysts for alkyne polymerization. Russo *et al.* employed palladium acetylides containing triphenylphosphine as catalysts for the polymerization of diethynylbiphenyl^[18], ethynylfluorene^[19] and ethynyltrimethylsilane^[20] to give polymers with molecular weights ranging from 10^3 to 10^4 . Kishimoto *et al.* reported the stereospecific living polymerization of phenylacetylenes using $\text{Rh}(\text{C}\equiv\text{CC}_6\text{H}_5)(\text{nbd})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ as catalyst^[1, 21]. We have accomplished polymerization of propargyl alcohol and its esters with novel palladium acetylide catalysts containing triphenylphosphine to give soluble polymers in high yields^[22-24].

This paper reports the results for homogeneous polymerization of *p*-diethynylbenzene (*p*-DEB) with nickel acetylide, *i.e.*, bis(triphenylphosphine)bis(*p*-ethynylphenylethynyl)nickel $[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2(\text{PPh}_3)_2, \text{Ni}-\text{C}]$, in 1,4-dioxane-toluene mixed solvents at room temperature. Soluble PDEB with a *trans* structure was

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obtained.

EXPERIMENTAL

Materials

All the solvents were analytical grade and dried with activated alumina. *p*-DEB and $\text{Ni}(\text{C} \equiv \text{CC}_6\text{H}_4\text{C} \equiv \text{CH})_2(\text{PPh}_3)_2$ were prepared according to the literature^[25, 26]. *p*-DEB was purified by sublimation before use.

Polymerization

All polymerization procedures were carried out under purified nitrogen atmosphere unless stated otherwise. A typical polymerization procedure is as follows: 378 mg (3 mmol) *p*-DEB and 25 mg (0.03 mmol) Ni—C were dissolved in 1,4-dioxane (1.25 mL) and toluene (1.25 mL) mixed solvents. Under purified nitrogen atmosphere, the polymerization proceeded at 25 °C for 5 h. The resulting polymer was precipitated by the addition of methanol, filtered off from the solution, washed with MeOH, and dried in vacuo at room temperature for 24 h to give PDEB.

For PDEB, ¹H-NMR (CDCl_3 , δ): 7.0–8.0 (*m*, 4H), 6.85 (*s*, 4/3H) and 2.8–3.3 (*m*, 2/3H). ¹³C-NMR (CDCl_3 , δ): 140, 139, 132, 130, 127, 120, 83 and 79. FT-IR (KBr, ν): 3293, 3031, 2106, 1603, 1500, 1440, 1400, 1250, 1100, 1070, 1018, 970, 910, 900, 840 and 520 cm^{-1} . UV (THF, λ_{max}): 250, 297 and 375. Elemental analysis for $(\text{C}_{10}\text{H}_6)_n$: (calcd.) C 95.24, H 4.76; (found) C 94.59, H 4.96%.

Measurements

IR spectrum of the polymer was taken on a Nicolet 5-DX FTIR spectrometer with KBr pellet. UV spectrum in THF was recorded on a Beckman DU-50 spectrophotometer. ¹H-NMR spectrum in CDCl_3 , using tetramethylsilane as internal standard was obtained with a Varian Unity 200 MHz NMR spectrometer. ¹³C-NMR spectrum was recorded in CDCl_3 solution on a Varian Unity 200 MHz NMR spectrometer. Elemental analysis was performed with a Carlo Erba Model 1106 elemental analyzer. The weight average molecular weight (M_w) and polydispersity index (M_w/M_n) of the polymer were measured on a Waters GPC Model 208 chromatograph at 30 °C, using THF as the eluent and standard polystyrene as the reference.

RESULTS AND DISCUSSION

Features of Polymerization

The effect of various solvents on the *p*-DEB polymerization initiated by Ni—C catalyst at 30 °C is shown in Table 1. The polymerization took place easily in aromatic solvents, DMSO, HNet₂, 1,4-dioxane, $\text{CH}_2\text{ClCH}_2\text{Cl}$ and CH_2Cl_2 , but hardly in DMF, THF, CHCl_3 and CCl_4 .

Table 1. Effect of solvents on *p*-DEB polymerization

Solvent	Solubility of PDEB in THF	Yield (%)
Toluene	Soluble	45.0
Xylene	Soluble	30.4
Benzene	Soluble	17.2
Chlorobenzene	Soluble	52.4
Phenetole	Soluble	32.3
HNet ₂	Partly Soluble	72.0
DMSO	Insoluble	81.2
1,4-Dioxane	Soluble	64.8
$\text{CH}_2\text{ClCH}_2\text{Cl}$	Soluble	66.1
CH_2Cl_2	Soluble	59.3
DMF	Soluble	4.0
THF	Soluble	4.8
CHCl_3	-	0
CCl_4	-	0

Conditions: catalyst concentration: $[\text{cat}] = 0.01 \text{ mol/L}$,
monomer concentration: $[\text{M}] = 1.0 \text{ mol/L}$, 30 °C, 6 h

Table 2 gives the yields of PDEB obtained from binary-component solvents. The yields of polymers are higher than those obtained from single-component solvents. It was found that 1,4-dioxane-toluene mixed solvents are favorable for the polymerization since the catalyst, monomer and polymer are all soluble in this mixed solvents, resulting in the formation of a homogeneous polymerization system and the soluble polymer.

Table 2. Effect of mixed solvents

Solvent	Solubility of PDEB in THF	Yield (%)
DMSO-toluene ^a	Hardly Soluble	98.2
HNEt ₂ -toluene	Hardly Soluble	81.2
1,4-Dioxane-toluene	Soluble	71.0
CH ₂ ClCH ₂ Cl-toluene	Soluble	68.4

^a $t = 0.5$ h

Conditions: volume ratio of solvents = 1, [cat] = 0.01 mol/L, [M] = 1.0 mol/L, 25°C, 6 h

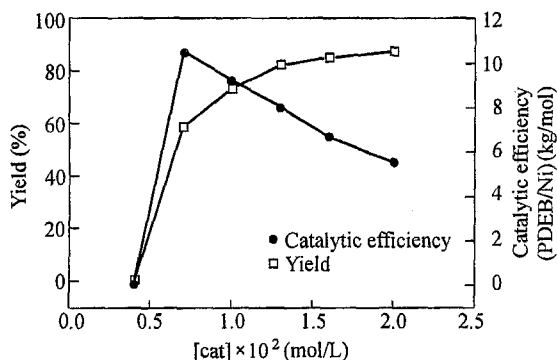
The influence of volume ratio of 1,4-dioxane/toluene (V_D/V_T) on the yield of PDEB was studied. As shown in Table 3, the yield reaches 71.0% at the optimum V_D/V_T of 1. When V_D/V_T is more or less than 1, the polymerization system is heterogeneous, and the yield decreases.

Table 3. Effect of volume ratio of 1,4-dioxane/toluene

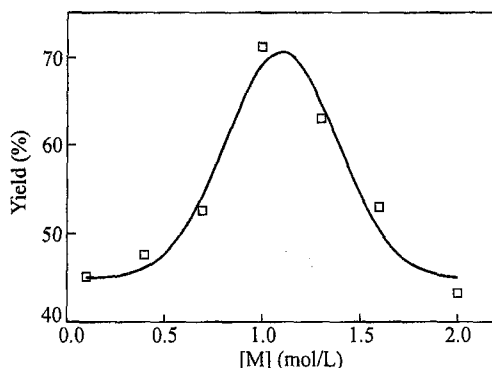
1,4-Dioxane/toluene (volume ratio)	Yield (%)
1/0	38.4
3/1	66.4
1/1	71.0
1/3	58.5
0/1	28.0

Conditions: [cat] = 0.01 mol/L, [M] = 1.0 mol/L, 25°C, 6 h

The Ni—C complex is an effective catalyst for *p*-DEB polymerization in a 1,4-dioxane-toluene mixed solvent system at 25°C. The effect of catalyst concentration on *p*-DEB polymerization is illustrated in Fig. 1. With increasing catalyst concentration, the yield increases while the catalytic efficiency decreases. Thus, for combination of high yield and catalytic efficiency, the optimum catalyst concentration is considered to be 0.01 mol/L. Figure 2 shows the effect of monomer concentration [M] on the yield. The optimum monomer concentration is 1.0 mol/L, corresponding to the highest yield of 71.0%.

**Fig. 1** Effect of catalyst concentration

Conditions: volume ratio of 1,4-dioxane/toluene = 1, [M] = 1.0 mol/L, 25°C, 6 h

**Fig. 2** Effect of monomer concentration

Conditions: volume ratio of 1,4-dioxane/toluene = 1, [cat] = 0.01 mol/L, 25°C, 6 h

It was observed that the yield and molecular weight of the polymer obtained with different electron donors containing N, O, P and Cl atoms added to the *p*-DEB polymerization system are different (Tables 4 and 5). NEt₃

and EtOH increase both the yield and molecular weight of PDEB. The optimum molar ratio of NEt_3 to $\text{Ni}-\text{C}$ catalyst is 3~5, under which the yield reaches 88% after polymerization for 5 h, and weight average molecular weight (M_w) reaches 2.4×10^4 , higher than that obtained without NEt_3 , but the polydispersity index becomes broader (M_w/M_n is as high as 8.2). Kishimoto^[1] also found that the additive containing N atom, *i.e.*, 4-(dimethylamino)pyridine, promoted the polymerization of phenylacetylene catalyzed by $\text{Rh}(\text{C}\equiv\text{CC}_6\text{H}_5)(2,5\text{-norbornadiene})(\text{PPh}_3)_2$. On the other hand, the polymerization hardly proceeded in the presence of PPh_3 and CCl_4 , but not for water. Kishimoto^[21] also observed that the reaction rate decreased markedly with increasing ratio of PPh_3 to catalyst in the polymerization of phenylacetylene with $[\text{Rh}(\text{OCH}_3)(2,5\text{-norbornadiene})_2]$ as the catalyst. The complex $\text{Ni}-\text{C}$ was decomposed by CCl_4 . These results indicate that the polymerization of *p*-DEB with $\text{Ni}-\text{C}$ catalyst does not belong to cationic and anionic polymerization.

Table 4. Effect of electron donor/ $\text{Ni}-\text{C}$ molar ratio

Electron donor/ $\text{Ni}-\text{C}$ (molar ratio)	Yield (%)					
	NEt_3	EtOH	H_2O	Phenetole	PPh_3	CCl_4
0	67.7	67.7	67.7	67.7	67.7	67.7
1	79.4	65.9	69.3	15.9	22.5	0
3	88.4	69.1	64.8	16.4	4.0	0
5	88.4	77.0	54.8	17.2	0	0
10	74.9	70.1	51.1	17.2	0	0
50	67.2	60.9	46.6	21.9	0	0

Conditions: volume ratio of 1,4-dioxane/toluene = 1, [cat] = 0.01 mol/L, [M] = 1.0 mol/L, 25°C, 5 h

Table 5. Influence of electron donors on the weight average molecular weight and polydispersity index of PDEB

Electron donor	M_w	M_w/M_n
—	3174	1.65
EtOH ^a	27061	8.61
NEt_3 ^a	23894	8.18
H_2O ^b	14071	5.86
PPh_3 ^b	3087	1.65

^a Electron donor/catalyst (molar ratio) = 5

^b Electron donor/catalyst (molar ratio) = 1

The effect of temperature on the *p*-DEB polymerization is significant, as shown in Table 6. The polymerization hardly proceeded below 20°C, but became so fast at above 40°C that gel-like and insoluble product was obtained. The optimum polymerization temperature is in the range of 25~30°C.

Table 6. Effect of polymerization temperature

T (°C)	Solubility of PDEB in THF	Yield (%)	M_w	M_w/M_n
0	—	—	—	—
10	Soluble	3.2	—	—
20	Soluble	15.3	2519	1.62
25	Soluble	67.5	3386	1.91
30	Soluble	70.1	3340	1.96
40	Mostly Soluble	78.3	5400	2.57
50	Partly Soluble	81.0	5677	2.73

Conditions: volume ratio of 1,4-dioxane/toluene = 1, [cat] = 0.01 mol/L, [M] = 1.0 mol/L, 3 h

Table 7 shows the effect of atmosphere gas on the *p*-DEB polymerization. The polymerization system exhibits high reaction activity under nitrogen atmosphere and low activity under air and hydrogen atmospheres. It is worth noticing that *p*-DEB can not be polymerized with $\text{Ni}-\text{C}$ catalyst under CO_2 atmosphere, probably due to the fact that carbon dioxide can insert into the nickel-carbon bond and coordinate with nickel to form a stable complex^[27], so that the monomer can no longer insert.

Table 7. Effect of atmosphere gas on *p*-DEB polymerization

Atmosphere gas	Yield (%)	M_w	M_w/M_n
N ₂	67.7	3174	1.65
Air	55.9	2992	1.60
H ₂	40.2	3518	1.77
CO ₂	0	—	—

Conditions: volume ratio of 1,4-dioxane/toluene = 1, [cat] = 0.01 mol/L, [M] = 1.0 mol/L, 25°C, 5 h

From the foregoing results, it is evident that the optimum conditions for *p*-DEB polymerization with Ni—C catalyst are as follows: [cat] = 0.01 mol/L, [M] = 1.0 mol/L, NEt₃/Ni—C (mol ratio) = 3~5, 1,4-dioxane/toluene (volume ratio) = 1 and $T = 25^\circ\text{C}$. Under such a condition, the yield and catalytic efficiency approach 88% and 11.1 kg PDEB/mol Ni, respectively after polymerization for 5 h.

Kinetic Behavior of Polymerization

The kinetic behavior of the *p*-DEB polymerization with Ni—C catalyst in 1,4-dioxane-toluene mixed solvent system at 25°C has been studied. Figure 3 shows a typical example of time-yield curve for the *p*-DEB polymerization. The yield increases linearly up to 3 h, and subsequently levels off.

The apparent polymerization rate (R_p) at different catalyst concentrations [cat] is calculated from the conversion measured in the initial stage at constant monomer concentration [M] = 1.0 mol/L. Figure 4 is a plot of $\lg[\text{cat}]$ versus $\lg R_p$ and indicates that $\lg R_p$ is in a linear relationship with $\lg[\text{cat}]$ having a slope of 2, *i.e.*, the polymerization is of second order with respect to [cat]. The polymerization rate is greatly dependent on the catalyst concentration. Figure 5 is a plot of polymerization time versus $-\ln(1-c)$ curves at different [cat]. It is evident that the polymerization is of first order with respect to [M] at the catalyst concentrations tested. Thus, the polymerization rate equation can be written as:

$$R_p = k_p[M][\text{cat}]^2 \quad (1)$$

where k_p , the apparent polymerization rate constant, is $0.47 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{S}^{-1}$ (25°C).

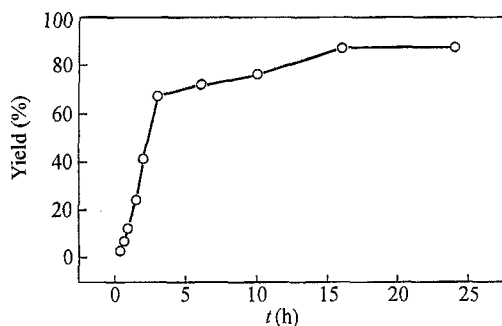


Fig. 3 A typical example of time-yield curve for the *p*-DEB polymerization
Conditions: volume ratio of 1,4-dioxane/toluene = 1, [cat] = 0.01 mol/L, [M] = 1.0 mol/L, 25°C

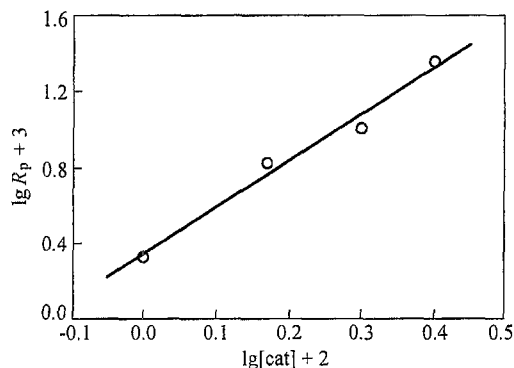


Fig. 4 Plot of $\lg[\text{cat}]$ versus $\lg R_p$
Conditions: volume ratio of 1,4-dioxane/toluene = 1, [M] = 1.0 mol/L, 25°C

Figure 6 shows the effect of polymerization temperature and indicates an Arrhenius-type dependence. Thus, the overall activation energy of *p*-DEB polymerization with Ni—C catalyst was estimated to be $203 \text{ kJ} \cdot \text{mol}^{-1}$, indicating great dependence of polymerization rate on the polymerization temperature.

The polymerization of *p*-DEB initiated by Ni—C complex follows a coordination insertion mechanism.

Polymers can be formed by the insertion of monomers into metal-carbon σ -bonds with the preliminary activation at the expense of π -complex formation. The polymerization mechanism has been studied in details in another contribution^[28].

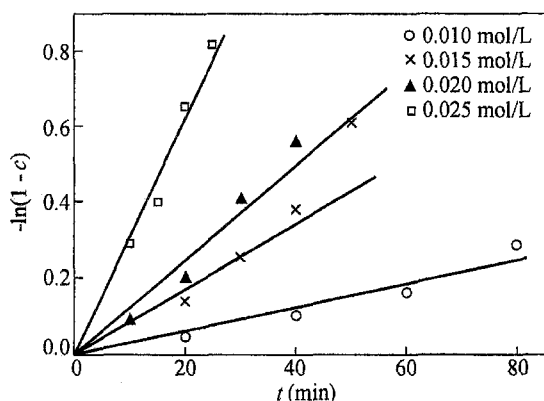


Fig. 5 Reaction time versus $-\ln(1-c)$ curves at different catalyst concentration [cat]
Conditions: volume ratio of 1,4-dioxane/toluene = 1, [M] = 1.0 mol/L, 25°C

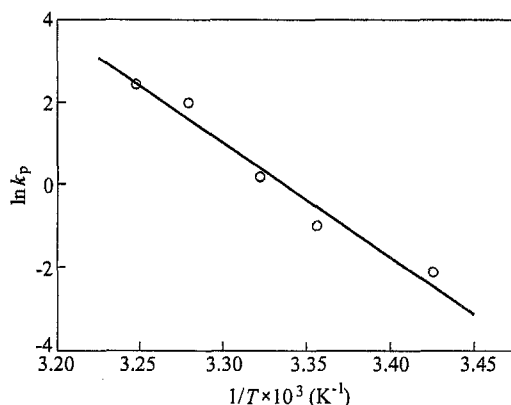


Fig. 6 Arrhenius plot of overall activation energy of *p*-DEB polymerization
Conditions: volume ratio of 1,4-dioxane/toluene = 1, [cat] = 0.01 mol/L, [M] = 1.0 mol/L

Characterization of PDEB

PDEB prepared is an orange colored powder and is soluble in THF, CHCl_3 and toluene. However, the polymerization conditions, such as solvent and temperature, exert a significant influence on the solubility of PDEB. If the polymerization is carried out in DMSO and HNet_2 or at high temperature, more than one triple bond per monomer will be cleared, and cross-linking reaction will happen, and the solubility of polymers will be decreased.

The IR spectrum of PDEB shows a characteristic absorption band at 1603 cm^{-1} ($\nu_{\text{C}=\text{C}}$), confirming the formation of an extended π -conjugated system. A $\nu_{\text{C}=\text{C}}$ band at 2106 cm^{-1} and a $\nu_{\text{C}=\text{C}-\text{H}}$ band at 3293 cm^{-1} are observable in the spectrum, indicating the presence of a large number of triple bonds in the polymer. Moreover, characteristic bands for *trans* structure ($1250, 1018, 970, 910\text{ cm}^{-1}$)^[29, 30] were also observed in the spectrum, while the bands for *cis* structure ($1380, 870, 740\text{ cm}^{-1}$)^[29, 30] are either very weak or absent. Thus, it is evident that PDEB has a rich-*trans* structure.

The *trans* extended π -conjugated polyene chain structure with the pendent groups of $p\text{-C}_6\text{H}_4\text{C}\equiv\text{CH}$ is further confirmed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra. The strong and broad signal at $\delta = 7.0\sim 8.0$ can be assigned to the aromatic protons. The peaks at $\delta = 2.8\sim 3.3$ are due to the protons of the pendent ethynyl groups. It is worth noting that the signal at $\delta = 5.82$, assigned to *cis* polyenic protons^[31], is absent, and that the signal at $\delta = 6.85$, assigned to *trans* polyenic protons^[31], is comparatively strong. The ratio of olefinic and aromatic protons to ethynylic protons is nearly equal to 8:1, so more than one triple bond per monomer molecule cleared during the polymerization, because the theoretical ratio should be 5:1 if only one acetylenic group per monomer molecule participated in the polymerization. The peak at $\delta = 127$ is attributed to CH group of *trans* vinylene units in analogy with poly(phenylacetylene)^[32]. The carbon signals from the ethynyl groups are at $\delta = 83$ and 79.

CONCLUSIONS

Nickel acetylide is an effective catalyst for the *p*-DEB polymerization, and the polymerization can proceed under mild conditions to give soluble rich-*trans* polymers with fairly high molecular weights in high yields. Polymerization conditions such as solvent, addition agent, atmosphere gas, catalyst and monomer concentration and polymerization temperature exhibit great influence on the polymerization.

REFERENCES

- 1 Kishimoto, Y., Eckerle, P., Miyatake, T., Ikariya, T. and Noyori, R., *J. Am. Chem. Soc.*, 1994, 116: 12131
- 2 Showa, Denko K.K., Hitachi, Ltd., 1984, Japanese Pat., 59 160, 965
- 3 Showa, Denko K. K., 1986, Japanese Pat., 61 174, 712
- 4 Asahi Chemical Industry Co., Ltd., 1985, Japanese Pat., 60 01, 211
- 5 Zhan, X.W., Yang, M.J. and Wan, M.X., *Synth. Met.*, 1998, 94: 249
- 6 Casalbore-Miceli, G., Camaioni, N., Yang, M.J., Zheng, M., Zhan, X.W. and D'Aprano, A., *Solid State Ionics*, 1997, 100: 217
- 7 Zhan, X.W., Yang, M.J., Lei, Z.Q., Li, Y., Liu, Y.Q., Yu, G. and Zhu, D.B., *Adv. Mater.*, 2000, 12: 51
- 8 Yu, G., Liu, Y.Q., Zhan, X.W., Li, H.Y., Yang, M.J. and Zhu, D.B., *Thin Solid Films*, 2000, 363: 126
- 9 Yang, Q.G., Si, J.H., Liu, X.C., Xu, G., Ye, P.X., Lei, Z.Q., Zhan, X.W. and Yang, M.J., *Chin. Phys. Lett.*, 1998, 15: 189
- 10 Yang, M.J., Li, Y., Zhan, X.W. and Ling, M.F., *J. Appl. Polym. Sci.*, 1999, 74: 2010
- 11 Yang, M.J., Li, Y., Zhan, X.W., Sun, H.M., Ling, M.F. and Zhu, Y.H., *Chin. Chem. Lett.*, 1998, 9: 223
- 12 Cherkashin, M.I., Kisilitsa, P.P. and Berlin, A.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 2450
- 13 Kapustyan, V.M., Zharov, A.A. and Enikolopyan, N.S., *Dokl. Akad. Nauk SSSR*, 1968, 179: 627
- 14 Broude, V.L., Gol'danskii, V.I. and Gordon, D.A., *Khim. Vys. Energ.*, 1968, 2: 165
- 15 Grovu-Ivanouiu, M., Bulacovschi, V. and Simionescu, C.I., *Makromol. Chem.*, 1985, 186: 2247
- 16 Gasparyan, G.T., Durgaryan, N.A., Ovakimyan, M.Z. and Indzhikyan, M.G., *Arm. Khim. Zh.*, 1988, 41: 716
- 17 Jabloner, H. and Cessna, J.L.C., *Polym. Prepr.*, 1976, 17: 169
- 18 Bolasco, A., Chimenti, F., Frezza, A., Furlani, A., Infante, G., Muraglia, E., Ortaggi, G., Polzonetti, G., Russo, M.V. and Sleiter, G., *Polymer*, 1992, 33: 3049
- 19 Russo, M.V., Iucci, G., Polzonetti, G. and Furlani, A., *Polymer*, 1992, 33: 4401
- 20 Russo, M.V., Furlani, A., Cuccu, A.M. and Polzonetti, G., *Polymer*, 1996, 37: 1715
- 21 Kishimoto, Y., Miyatake, T., Ikariya, T. and Noyori, R., *Macromolecules*, 1996, 29: 5054
- 22 Yang, M.J., Zheng, M., Furlani, A. and Russo, M.V., *J. Polym. Sci.: Part A: Polym. Chem.*, 1994, 32: 2709
- 23 Yang, M.J., Sun, H.M. and Ling, M.F., *Acta Polym. Sinica*, 2000, (2): 161
- 24 Sun, H.M. and Yang, M.J., *Chin. Chem. Lett.*, 2000, 11: 1097
- 25 Hay, A.S., *J. Org. Chem.*, 1960, 25: 637
- 26 Nast, R. and Beyer, A., *J. Organometal. Chem.*, 1981, 204: 267
- 27 Zakharov, V.A., Bukatov, G.D., Chumaevshii, N.B. and Yermakov, Y.I., *React. Kinet. Catal. Lett.*, 1974, 1: 247
- 28 Zhan, X.W. and Yang, M.J., *J. Mol. Catal. A: Chem.*, 2001, 169: 57
- 29 Simionescu, C., Dumitrescu, S.V. and Percec, V., *J. Polym. Sci.: Polym. Symp.*, 1978, 64: 209
- 30 Chien, J.C.W., "Polyacetylene", Academic Press, New York, 1984
- 31 Simionescu, C.I. and Percec, V., *J. Polym. Sci.: Polym. Symp.*, 1980, 67: 43
- 32 Percec, V. and Rinaldi, P., *Polym. Bull.*, 1983, 9: 548