

SYNTHESIS OF THE COPOLYMERS OF p-DIETHYNYLBENZENE WITH OTHER ACETYLENIC DERIVATIVES INITIATED BY $(\text{Ph}_3\text{P})_2\text{PdCl}_2$

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ABSTRACT

The copolymerization of p-diethynylbenzene (PDEB) with phenylacetylene (PhA), 4,4'-diethynylbiphenyl (DEBP) or m-diethynylbenzene (MDEB) are studied by varying mole ratios of monomers. When the mole ratios of PDEB/PhA are less or equal to 1/5, the copolymers are soluble and fusible, but the other copolymers are insoluble and infusible. The results show that the good solvent of cross-linked copolymers is benzene and their solubility parameter is $9.15 \text{ cal}^{0.5} \cdot \text{cm}^{-1.5}$. And their swellability (θ_p), Huggins parameter (χ), density (d_4^{25}) and the average molecular weights between crosslinks ($\overline{M}_c$) are measured. It is found that θ_p and $\overline{M}_c$ of copolymers are greater but d_4^{25} is less than that of respective homopolymers. IR spectra show that the copolymers have transoid configuration and small number of unreacted ethynyl groups exist in the copolymers. The mechanism about the polymerization of acetylenic derivatives initiated by $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ is discussed.

INTRODUCTION

p-Diethynylbenzene (PDEB) can be polymerized by using the methods of catalytic polymerization^[1,2], electroinitiated polymerization^[3] and photocatalysis polymerization^[4]. The polymer obtained, poly(p-diethynylbenzene) (PPDEB) can form crosslinked thermosetting composites which are suitable for the manufacture of ablative coating for space vehicle, aircraft wing edges, bearing and so on^[5]. And this kind of thermoset resin is abrasion-, chemical- and high temperature-resistant. In order to improve its properties, the method of copolymerization is often used and there have been many reports about the copolymerization of PDEB with other acetylenic derivatives^[6,7].

In this paper, the copolymers of PDEB/phenylacetylene (PDEB/PhA), PDEB/4,4'-diethynylbiphenyl (PDEB/DEBP) and PDEB/m-diethynylbenzene (PDEB/MDEB), are prepared by using $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ as the catalyst. The good solvent of these crosslinked copolymers is selected and the swellability, the solubility parameters, Huggins parameter and the average molecular weights between crosslinks are measured. And their infrared spectra are reported.

EXPERIMENTS

Materials

Biphenyl, benzene, Ph_3P , chloroform and styrene are chemical grade reagents. PdCl_2 is analytically pure reagent. The divinylbenzene is industrial grade reagent

with the content of only 40% and separated by the method of Cu_2Cl_2 complex^[8] before use.

Monomers and catalyst syntheses

(1) PDEB and MDEB are prepared from divinylbenzene, PhA from styrene and DEBP from biphenyl according to the literature method^[9].

(2) $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ is prepared from PdCl_2 and Ph_3P according to the literature method^[10].

Polymers and copolymers syntheses

The weighed monomers (or monomer) and $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ (here, the mole ratio of $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ /monomers is 1/100) are added into a tube heated in an oil bath. When heated up to certain temperature, the vigorous polymerization reaction occurs. After about 10 seconds, the reaction becomes alleviated voluntarily. At the reaction temperature, the reaction mass of copolymer (or polymer) is kept in the oil bath for an hour, and then the polymer product is kept in a dryer.

Measurements

The determination of the good solvent for the polymers and the measurements of the swellability (θ_p), the solubility parameter (δ_p), density (d_4^{25}) and the average molecular weights between crosslinks ($\overline{M}_c$) of the products are done according to the literature method^[11]. Huggins parameter (χ) is determined according to the literature method^[12].

Infrared spectra of the products are recorded on an Infrared Spectrophotometer of HITACHI 270-model.

RESULTS AND DISCUSSIONS

Preparation of copolymers of PDEB/PhA

The results of copolymerization of PDEB/PhA in various mole ratios are listed in Table 1. From Table 1, it is clear that the temperatures of copolymerization of PDEB/PhA are lower than that of homopolymerization of PDEB or PhA; when the mole ratio of PDEB/PhA is greater than or equal to 1/2, the products are insoluble and infusible; when that is less than or equal to 1/10, the products are soluble and fusible and when that is equal to 1/5, the products can be separated into two categories, the former is insoluble but fusible while the latter is soluble and fusible. Moreover, as the mole ratio of PDEB/PhA increases, the colour of the products become dark, the swellability of the products and the average molecular weights between crosslinks increase and the density of the products increases, too.

Preparation of copolymers of PDEB/DEBP

The data of the copolymerization of PDEB/DEBP in various mole ratios are listed in Table 2. It can be seen that the temperatures of the copolymerization of PDEB/DEBP is between the temperatures of the respective homopolymerization of PDEB and DEBP, the swellability and the average molecular weights between crosslinks of the copolymers are larger than that of the homopolymers of PDEB or DEBP, but the density of the copolymers is less than that of their homopolymers. Because of the crosslinkage of molecules, the copolymers and homopolymers are insoluble and infusible.

Preparation of copolymers of PDEB/MDEB

Table 1 The results of the copolymerization of PDEB/PhA

PDEB/PhA (mole ratio)	Temp. ^{a)} (°C)	Yield (%)	m.r. ^{b)} (°C)	Product colour ^{a)}	Solubility ^{d)}	$\theta_p^c)$	d_4^{25}	$\overline{M}_c$
pure PDEB	238	94.5	infusible	d — b	insoluble	1.351	1.097	190
1/1	77	94.6	infusible	d — b	insoluble	1.796	1.039	410
1/2	75	93.8	infusible	d — b	insoluble	1.814	1.030	420
1/5	70	20.0	280 — 320	d — b	insoluble	1.979	1.020	515
		74.9	112 — 117	o — b	soluble			
1/10	65	96.0	135 — 142	o — b	soluble			
pure PhA	100	92.9	120 — 127	o — b	soluble			

a. Temperature when the reaction occurs.

b. melting range. Infusible represents that the product does not melt when heated up to 350°C

c. d.b and o represent dark, brown and orange respectively.

d. The solvents are benzene, CHCl₃, THF and so on.

e. The swellability of the products.

Table 2 The results of the copolymerization of PDEB/DEBP^{a)}

PDEB/DEBP (mole ratio)	Temp. (°C)	Yield (%)	Product colour	θ_p	d_4^{25}	$\overline{M}_c$	Solubility and m.p.(°C)
2/1	146	92.1	b.	3.043	1.091	1398	All products are insoluble in all organic solvents and water and infusible when heated up to 350 °C .
1/1	178	92.8	b.	2.863	1.102	1250	
1/2	172	94.6	b.	3.687	1.082	2000	
pure DEBP ^{b)}	120	97.0	b.	1.416	1.135	230	

a) All symbols in Table 2 and 3 are the same with that in Table 1.

b) The best solvent of the polymer of pure DEBP is THF and these data are measured in THF.

Table 3 The results of the copolymerization of PDEB/MDEB

PDEB/MDEB (mole ratio)	Temp. (°C)	Yield (%)	Product colour	θ_p	d_4^{25}	$\overline{M}_c$	Solubility and m.p. (°C)
2/1	178	92.1	b.	2.247	1.061	720	all products are insoluble in all organic solvents and water and infusible when heated up to 350 °C .
1/1	174	96.0	b.	2.210	1.059	687	
1/2	169	90.4	b.	2.208	1.068	795	
pure MDEB	230	98.1	b.	1.486	1.130	265	

The results of copolymerization of PDEB/MDEB in various mole ratios are presented in Table 3. From Table 3, the temperatures of the copolymerization of PDEB/MDEB are lower than that of their respective homopolymerization, and the swellability and the average molecular weights between crosslinks of copolymers are larger than those of their homopolymers, but the density of the copolymers is lower than that of their homopolymers. Generally, the yield of all products is very high.

Solubility parameter of the products

A group of solvents, which have different solubility parameter (δ_s), is selected^[13] to measure the swellability of some representative polymers and copolymers. The results are showed in Figures 1,2 and 3. It can be found that the

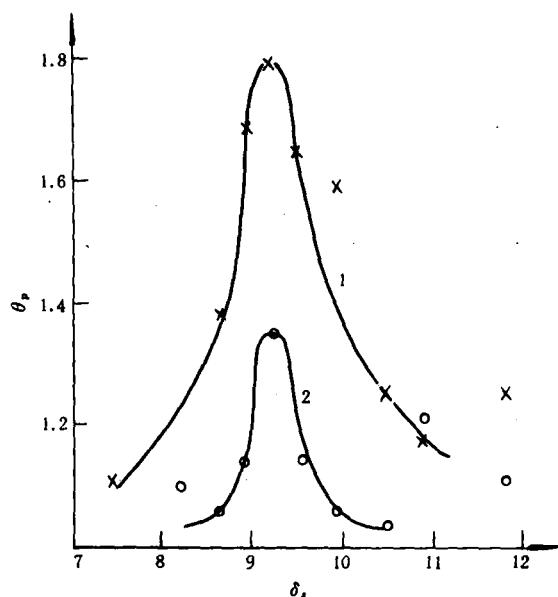


Fig.1 The relation curves of the swellability θ_p of the products and the solubility parameter δ_s of solvents. (1. The copolymer of PDEB/PhA(1/2); 2. PPDEB).

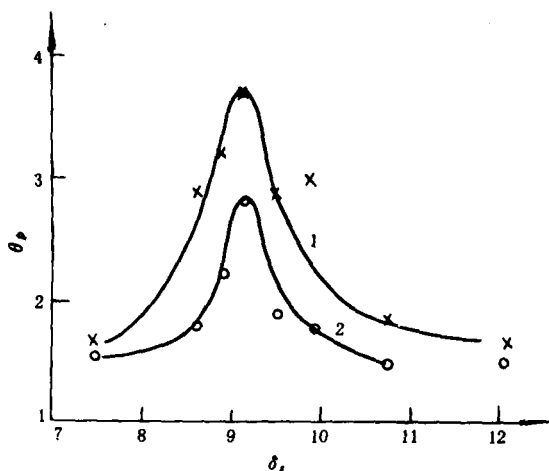


Fig.2 The relation curves of the swellability θ_p of the products and the solubility parameter δ_s of the solvents. (1. The copolymer of PDEB/DEBP (1/2); 2. The copolymer of PDEB/DEBP (1/1))

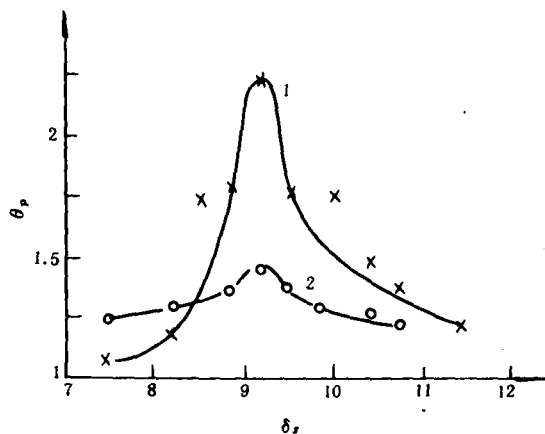


Fig.3 The relation curves of the swellability θ_p of the products and the solubility parameter δ_s of the solvents. (1. The copolymer of PDEB/MDEB; 2. PMDEB)

good solvent of these products is benzene. Because the solubility parameter of benzene is $9.15 \text{ cal}^{0.5} \cdot \text{cm}^{-1.5}$, the solubility parameter of all products can be approximately believed as $9.15 \text{ cal}^{0.5} \cdot \text{cm}^{-1.5}$ except poly (DEBP). The best solvent of poly (DEBP) is THF^[14] and its solubility parameter is $9.9 \text{ cal}^{0.5} \cdot \text{cm}^{-1.5}$.

According to Bristow's equation^[12], Huggins parameter (χ) is presented as

$$\chi = 0.34 + V_s / RT (\delta_s - \delta_p)^2 \quad (1)$$

Here, δ_s is the solubility parameter of solvent;

δ_p is the solubility parameter of polymer (or copolymer);

V_s is the mole volume of solvent;

R is the gas constant;

T is the Kelvin temperature.

If the best solvent of copolymers (i.e. benzene) is selected to measure their swellability, the Huggins parameter of copolymers is 0.34. After the density of copolymers is measured, the average molecular weights between crosslinks ($\overline{M}_c$) can be calculated according to the following equation:

$$\overline{M}_c = -\rho_2 V_s \phi_2^{2/3} / (\ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2) \quad (2)$$

Here, ρ_2 is the density of copolymer, i.e. d_4^{25} ;

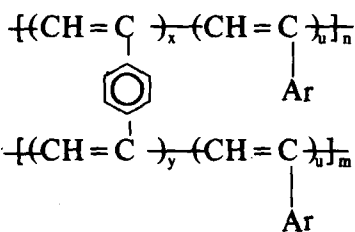
ϕ_2 is $1/\theta_p$, θ_p is the swellability of copolymer;

V_s is the mole volume of solvent;

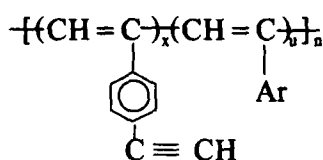
χ is Huggins parameter.

The Infrared spectra of the products

The structures of the products may be 1 or 2:



structure 1



structure 2

Here, Ar is aryl group and if there is ethynyl group in Ar, the ethynyl group has reacted; x, y, u and v are greater than or equal to 1 respectively; if u and v are zero respectively, the polymer is PPDEB and if x and y are zero respectively, the product is the homopolymer of PhA or MDEB or DEBP.

The infrared spectra of the copolymers of PDEB/PhA are shown in Fig 4. The monosubstituted benzene has strong characteristic peaks on 700cm^{-1} and 750cm^{-1} in IR spectra while the para-disubstitution benzene at 830cm^{-1} . And the copolymers of PDEB/PhA have the characteristic peaks at 700cm^{-1} , 750cm^{-1} and 830cm^{-1} and the absorption strength of these three peaks occurs regularly changing with the change of mole ratios of PDEB/PhA, the larger the mole ratio of PDEB/PhA, the stronger the absorption strength at 830cm^{-1} , and otherwise, the weaker the absorption strength at 830cm^{-1} is.

Then there is a characteristic peak at 3300cm^{-1} in the case of curves of a, b and c and this is related to the vibration of $\text{H}-\text{C}\equiv$ and shows that while the mole ratio of PDEB/PhA is greater than or equal to $1/2$, the ethynyl groups have not completely reacted. This shows that when the mole ratio of PDEB/PhA is greater than or equal to $1/2$, the structure of the copolymers may be the structure 1 and the structure 2 unit exists in the structure 1, the unreacted ethynyl groups are randomly distributed in the copolymers. When the mole ratio of PDEB/PhA is less than or equal to $1/5$, the structure of the copolymers is the structure 1 and all ethynyl groups have reacted.

Moreover, the absorption peak at 920cm^{-1} is stronger than that at 895cm^{-1}

and the absorption peak at 1500cm^{-1} is stronger than that at 1450cm^{-1} , these show that the microstructure of the main chain in the copolymers is trans configuration^[15].

Figure 5 is IR spectra of the copolymers of PDEB/DEBP. PPDEB and PDEBP all have a characteristic peak at 1000cm^{-1} , but this peak of their copolymers divides into doublet (at 1000cm^{-1} and 1020cm^{-1}). The peak of the copolymers and PDEBP at 3300cm^{-1} shows that there are unreacted ethynyl groups in the copolymers, i.e., the structure 2 unit exists in structure 1, which

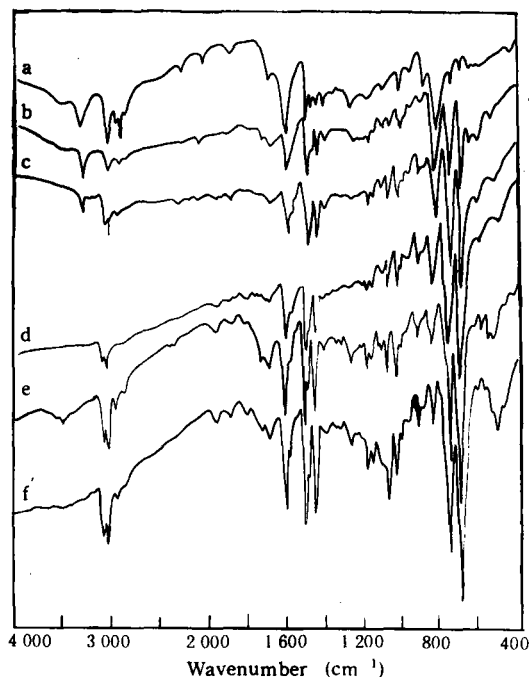


Fig.4 The IR spectra of the copolymers of PDEB / PhA

a. PPDEB; b,c,d,e and f are the copolymers with the mole ratios of 1/1, 1/2, 1/5, 1/5 and 1/10 respectively; d is fusible but insoluble and e is soluble and fusible.

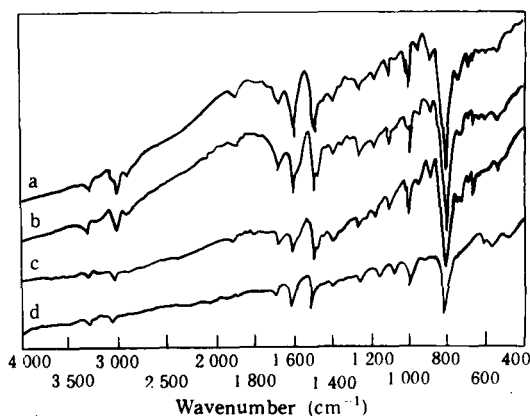


Fig.5 The IR spectra of the copolymers of PDEB / DEBP. a,b and c are the copolymers with the mole ratios of 2/1, 1/1 and 1/2 respectively; d is PDEBP

may be the structure of copolymers. Moreover, the characteristic peak at 830cm^{-1} is attributed to the absorption of para-disubstitution benzene and that at 3030cm^{-1} is attributed to the absorption of the C—H bond on benzene ring.

Figure 6 is the IR spectra of the copolymers of PDEB/MDEB. PPDEB has a characteristic peak at 830cm^{-1} while PMDEB has two peaks at 700cm^{-1} and 800cm^{-1} , and the copolymers of PDEB/MDEB have three peaks at 700cm^{-1} , 800cm^{-1} and 830cm^{-1} . Furthermore, the larger the mole ratio of PDEB/MDEB the stronger the characteristic peak of PPDEB at 830cm^{-1} is, and vice versa.

Moreover, the peaks at 3300cm^{-1} and 2200cm^{-1} for the copolymers show that there are unreacted ethynyl groups in these products. Therefore, the microstructure of the copolymers may be the structure 1 and the structure 2 exists randomly in the main chain of structure 1.

Polymerization mechanism

When $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ is used in the polymerization of PhA, *trans-cis* polyphenylacetylene (PPhA) can be obtained^[15]. In this paper, the *transoid* copolymers of PDEB/PhA have been obtained. Therefore, the copolymerization of PDEB with other acetylenic derivatives may follow the metathesis mechanism

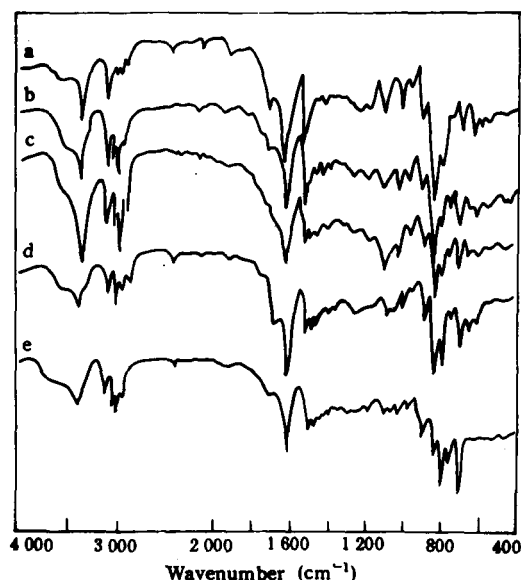
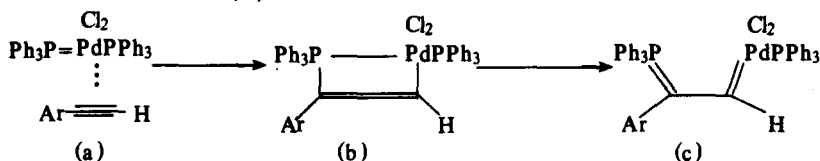


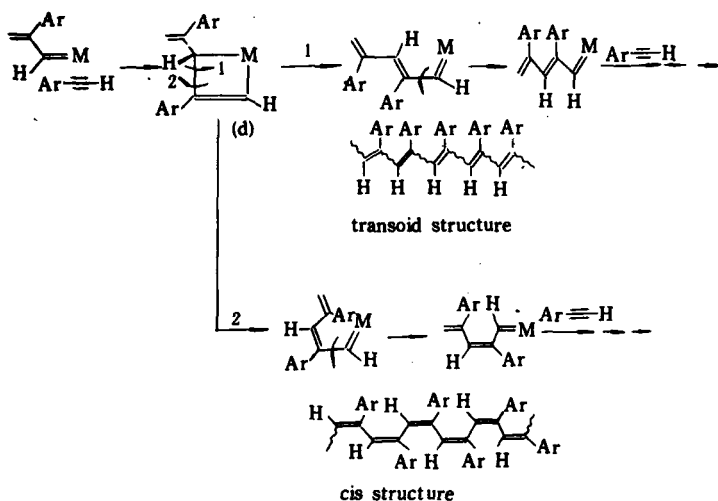
Fig.6 The IR spectra of the copolymers of PDEB/MDEB
a,b,c and d are the copolymers and the mole ratios of monomers are in the order of 2/1, 1/1, 1/1 and 1/2; c is the product of thermopolymerization under 250 °C ; e is PMDEB.

presented by Katz^[16].

At first, the ethynyl group with $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ forms π -complex (a), and the π -complex then forms the metallacyclobutene intermediate (b) and the intermediate further forms metal carbene (c):

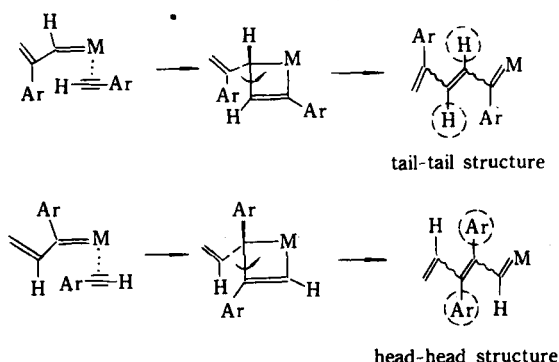


The metal carbene has a high activity and can immediately start the chain propagation reaction:



Here, M represents $\text{Ph}_3\text{PPdCl}_2$ group; Ar represents aryl; if there is ethynyl group in Ar, the ethynyl group can also react.

The geometric structure of copolymers depends on the rotational direction of metallacyclobutene intermediate (d). The rotation should be in such a route as to minimize the steric interaction between the coordinated metal ($\text{Ph}_3\text{PPdCl}_2$) and substituents, i.e. Ar or H or polymer backbone. Following the route 1, the steric interaction between $\text{Ph}_3\text{PPdCl}_2$ and H is less than that between $\text{Ph}_3\text{PPdCl}_2$ and polymer backbone in the case of following the way 2. Therefore the copolymers obtained are mainly trans ones. Of course, the copolymers showed by the equation above, are head-tail structure only, and because this reaction proceeds very fast, it is possible that there are head-head and tail-tail structures in the main chains of these copolymers according to the following equation:



The head-tail, head-head and tail-tail structures exist randomly in the main chains of the copolymers and small number of unreacted ethynyl groups with aromatic nucleus hang on the main chains of the copolymers. This may be the practical structure model of these copolymers.

Keywords:

p-Diethynylbenzene, Phenylacetylene, 4,4'-Diethynylbiphenyl, m-diethynylbenzene

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