Polymer Vol. 37 No. 16, pp. 3763-3765, 1996
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0032-3861/96/$15.00+0.00

S0032-3861(96)00189-9

Study on whole-conjugated polymer gel. Synthesis of polybenzal gel with benzal chloride and toluene

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(Received 21 August 1995; revised 17 November 1995)

Polybenzal (*m*-directing) gels were synthesized with benzal chloride (BC, monomer and crosslinking agent), toluene (monomer), and anhydrous aluminium chloride (catalyst) in nitrobenzene at 90°C by the Friedel-Crafts alkylation. The colour of the product changed from brown to black as the toluene content decreased. The swelling of the product gel in tetrahydrofuran was slight or none. No gelation occurred in the case of the molar ratio of toluene/BC above 0.75. Considering the above results, i.r. spectra, visible spectra, and composition of the products, the polymer gels obtained had many long conjugated systems. Copyright © 1996 Elsevier Science Ltd.

(Keywords: whole-conjugated polymer gel; *m*-directing polybenzal; Friedel-Crafts alkylation)

Introduction

Recently, many studies on conducting polymers have been reported. Synthesis of polyphenylene was especially noted because of the higher stability to air, heat, and light than other conjugated polymers such as polyacetylene. However, it is difficult to synthesize polyphenylene with a higher molecular weight and long conjugated system: the polycondensation direction should be *ortho* or *para* not *meta*. Also, it is not easily applied to conducting or semi-conducting electrical materials because the electrical resistance among polymer chains is high in spite of good conductivity along a polymer chain. If each polymer chain is crosslinked by the group continuing each conjugated system, then electrical resistance among the polymer chains will become low although the polymer becomes insoluble in solvent (polymer gel).

Some workers reported the synthesis of polybenzyl with benzyl chloride (BC) or xylenyl dichloride by the Friedel-Crafts reaction[1-3]. If in this reaction BC or a mixture of BC and toluene is used, *meta*-directing polybenzal (PBza) gel will be obtained (see *Figure 1a*). This reaction will be able to proceed because triphenylmethane can be synthesized with chloroform and benzene, PBza gel will be a whole-conjugated polymer because the conjugated systems continue by the side-by-side crosslinking between two end groups (see *Figure 1b*). In order to continue the conjugated system, the polycondensation direction should be *meta* not *ortho* or *para*. In the Friedel-Crafts alkylation, *meta*-directing alkylation proceeds predominantly by use of anhydrous aluminium chloride ($AlCl_3$) as a catalyst (most active catalyst for Friedel-Crafts alkylation) at high temperature. In this gel, the crosslinking density is determined by the toluene content. If the crosslinking density is low, the side-by-side continuing conjugated system and its electrical conductivity will decrease. Then, PBza gel can be applied to semi-conducting electrical materials by changing the toluene content.

In this study, PBza gel was synthesized with BC (monomer and crosslinking agent) and toluene (monomer with various mol-content) by Friedel-Crafts alkylation to yield a whole-conjugated polymer gel.

Experimental

Materials. BC, nitrobenzene and toluene were purified by distillation. Anhydrous $AlCl_3$ was a commercial product used without further purification.

Polycondensation procedure. Nitrobenzene (30 ml) and anhydrous aluminium chloride ($AlCl_3$, about 0.05 mol) were put into two-necked flasks. An exit tube designed to lead evolved hydrogen chloride into aq NaOH was fitted to one neck. A dropping funnel was fitted to the other neck. The mixture of BC (8.05 g, 0.05 mol) and toluene with various molar ratios was added from the funnel to the nitrobenzene-$AlCl_3$ mixture at 90°C with stirring. After addition, the reaction mixture was kept at 90°C for 10 h. After the reaction, aq NaOH was poured into the reaction mixture and $AlCl_3$ was deactivated. The aluminium compound was dissolved with excess aq NaOH and the precipitate (gel) filtered: in the case of no gelation, the polymer-nitrobenzene solution was separated from the aqueous layer and mixed with methanol, and the precipitate was purified by reprecipitation with a tetrahydrofuran (THF)-methanol system. Nitrobenzene was removed

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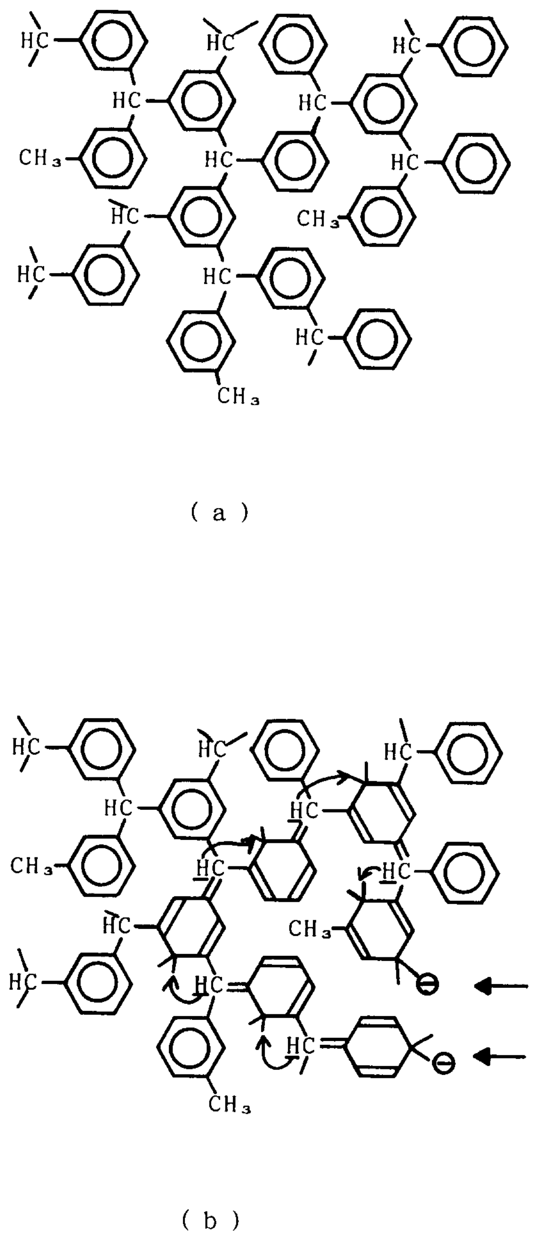

Figure 1 Structures of PBza gel: (a) PBza gel; (b) conjugated system of PBza gel as an example

with methanol and some impurities were also extracted by using a Soxhlet extractor for 6 h with THF. The purified product was dried in vacuum at 100°C.

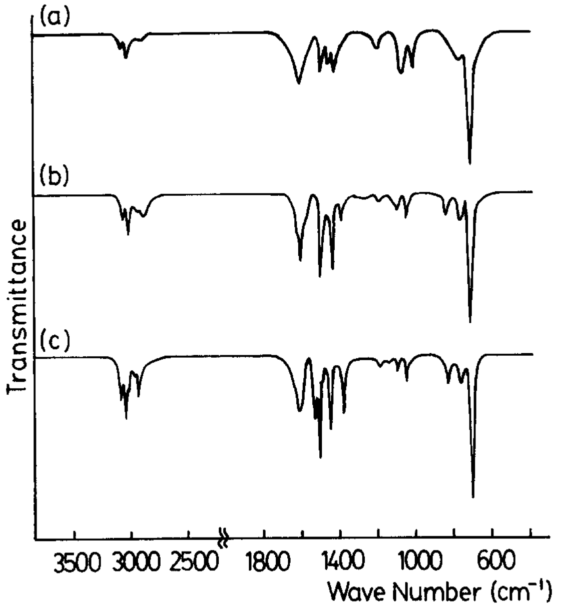

Figure 2 I.r. spectra of PBza gels: (a) PBza1; (b) PBza3; (c) PBza6 (soluble in THF)

Characterization. Infrared (i.r.) spectra were taken on an Hitachi 260-30 IR spectophotometer. The ratio of *meta*-linkage in the methine–phenyl–methine linkage was calculated from the ratio of peak area of the i.r. spectrum as:

$$\text{ratio of } meta\text{-linkage} = \frac{\text{area of } 700\,\text{cm}^{-1}}{\text{area of } 700\,\text{cm}^{-1} + \text{area of } 800\,\text{cm}^{-1}}$$

The 800 and 700 cm^{-1} peaks in the i.r. spectrum correspond to *ortho*- or *para*-linkage, and *meta*-linkage, respectively. The i.r. calibration was made from the i.r. measurement of the mixture of *p*-xylene and *m*-xylene. The composition of BC and toluene in the product was determined by comparing the peak area at 1380 cm^{-1} (methyl group of toluene) and 1600 cm^{-1} (phenyl group of BC and toluene) in the i.r. spectra: the ratio of methyl group/phenyl group was then calculated. The i.r. calibration was made by the spectra of the mixture of 1,2,4,5-tetramethylbenzene and triphenylmethane with various compositions. Visible spectra were taken on a Shimazu UV-200 Double Beam Spectrophotometer (wavelength 400–900 nm). For soluble products in THF, visible measurements were carried out with the THF solutions. For gel products the measurements were done with a finely powdered product which was placed between two glass plates under the microscope. The swelling property of PBza gel was observed in THF.

Results and discussion

Upon polymerization, the colour of the reaction mixture changed immediately to deep red from light yellow (nitrobenzene) when the mixture of BC and toluene was dropped into the $AlCl_3$–nitrobenzene mixture. This is the characteristic colour of polymerization by Friedel–Crafts alkylation[2]. The colour then changed immediately from red to dark blue and dark black and gelation occurred in PBza1–PBza14. This change of colour means that long conjugated systems are formed.

Figure 2 shows the i.r. spectra of PBza1, PBza3, and PBza6. In *Figure 2*, the peaks of the methine group (1080 cm^{-1}) and methyl group (2900, 1380 cm^{-1}) are observed. The peaks of the methyl group (especially at 1380 cm^{-1}) become sharp and large as the toluene content increases. It is found that the alkyl dichloride group of BC reacted nearly completely as a peak near 1200 cm^{-1} corresponding to the -$CHCl_2$ or -CHCl-group is only slightly observed. At 700 cm^{-1}, a sharp peak corresponding to *meta*-disubstituted alkyl benzene and monosubstituted benzene is observed and any peak near 800 cm^{-1} corresponding to *ortho*- or *para*-disubstituted alkyl benzene is slightly observed.

Table 1 lists the feed molar ratio, synthesis results, and characteristics of PBza gels. The gelation occurred when

Table 1 Feed ratio of monomer, synthesis results, and characteristics of PBza gels[a]

Run no.	Feed ratio[b]		Yield (%)		Colour		Degree of swelling[d]	Composition[e] toluene/BC (mol/mol)	Ratio of *meta*-linkage[f]
	Toluene/BC (mol/mol)	Gelation[c]	Gel	Soluble part in THF	Gel	Soluble part in THF			
PBza1	0	○	88.7	None	Dark black	—	None	0	0.99
PBza2	0.1	○	64.3	Small amount	Dark brown	Dark brown	None	0.11	0.93
PBza3	0.25	○	70.9	Small amount	Dark brown	Dark brown	None	0.32	0.92
PBza4	0.5	○	64.4	3.4	Brown	Brown	Slight	1.00	0.94
PBza5	0.75	×	None	60.1	Black	Black	Soluble	1.20	—
PBza6	1.0	×	None	29.7	Black	Black	Soluble	4.71	—

[a] Reacted in nitrobenzene at 90°C for 10 h
[b] Molar ratio
[c] ○, gelation; ×, no gelation
[d] In THF
[e] From i.r. measurement, PBza1–PBza4: gel part, PBza5–PBza6: soluble part in THF
[f] Ratio of *meta*-linkage in all methine–phenyl–methine linkages, determined by i.r. measurement

the molar ratio of toluene/BC was less than 0.5. The gelation should occur theoretically when the ratio is less than 1.0; but no gelation was observed in PBza5 and PBza6. Then the soluble part in THF (3.4%) was also obtained in PBza4. In PBza5 the molar ratio was 0.75, the condensation intermediate has some reactive chlorine groups. If these chlorines are used in the next reaction, gelation may occur; but if the intermediate has no available chlorine with increasing of the intramolecular reaction, no further reaction occurs. When the molar ratio is near to 1 : 1, the remaining reactive chlorines are few. Therefore, gelation did not occur in PBza5, PBza6, and only partially in PBza4. In this reaction, the usual gelation theory cannot be adapted because the number of *m*-positions which can be substituted by -CHCl$_2$ or -CHCl- groups is two in both BC and toluene. However only BC has alkyl chloride groups. In addition, in this experiment, the Friedel–Crafts alkylation proceeded rapidly, and the reaction did not proceed ideally.

The colour of PBza gel becomes dark with increase in toluene content, while PBza1 and PBza2 are slightly bluish dark black with a metallic lustre like 'coke'. Hydrocarbon compounds are usually colourless or white except for some polycyclic condensed hydrocarbons, polyacetylenes, and polyphenylenes. Usually, when the conjugated system in an organic compound becomes long, its colour changes from colourless or red to blue, violet, or black, and becomes 'deep' and 'dark'. In comparison with PBza1–PBza4, the conjugated system of PBza1 is long because many conjugated side-by-side links exist due to lack of toluene. In PBza5 and PBza6, the soluble part in THF is black though gelation did not occur in this series. It is found that these products also have long conjugated systems. In PBza1–PBza3, the swelling in THF cannot be observed and even in PBza4, the swelling is slight. These phenomena are due to the rigid structure of PBza gel shown in *Figure 1*. In this structure, *m*-directing phenylene and methine groups are linked alternatively in the main chain. It is thus difficult to alter the conformation of the main chain with solvent and so the chain cannot be expanded. The composition of toluene/BC (mol/mol) of the product nearly corresponds to the feed ratio of monomer. It is found that the composition increases in proportion to the feed ratio of toluene, though it is thought that these values contain many errors. The ratio of *meta*-linkage in the methine–phenyl–methine linkage is more than 0.9. The PBza gels obtained consist almost of *meta*-linkages among the methine–phenylene–methine groups.

From the visible spectra of PBza gels (PBza1–PBza3), the absorption of light is observed in all visible regions and the longer wavelength regions (> 700 nm). The absorbance increases slightly in all samples as the wavelength elongates. The phenomenon becomes noticeable during decrease of the toluene mol-content. This means that many long conjugated systems of various lengths exist in the gel and that long conjugated systems exist more in the lower mol-content PBza. From the visible spectra of soluble PBza in THF (PBza4–PBza6), the absorption decreases in all samples as wavelength increases, in contrast to that of PBza gels. This results shows that the soluble PBza5, PBza6 and, in part, PBza4 have shorter conjugated systems in comparison with the PBza gels.

From these results, the PBza gel obtained has many long conjugated systems. The electric properties of the PBza gel will be reported in the near future.

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