Study of Crosslinking of Polyphosphazene with Allyl Pendant Groups Initiated by Benzoyl Peroxide

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ABSTRACT: A selected polyorganophosphazene containing three substituents: phenoxy group, 2-allylphenoxy group, and ethoxy group, had been thermally cross-linked. The polymer can be crosslinked at 85°C which was lower than the general reported operation temperature. The transformation of chemical structure was analyzed by FTIR technique. It was found that oxidization caused the formation of peroxides, ether and ester during crosslinking. The effect of different conditions including time, temperature, and initiator on properties of crosslinked polymer had been studied. The change of properties was well consistent with the change of chemical structure including vinyl and peroxide. Detailed cross-linking mechanisms were proposed based on FTIR spectra by monitoring the possible association sites. It was suggested that the initiation reaction preferentially occurred at methylene but not vinyl, and major linkages between polymer chains were ether and peroxide bonds. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2353–2360, 2009

Key words: polyphosphazene; membrane; crosslinking; benzoyl peroxide

INTRODUCTION

Polyphosphazenes are linear polymers containing an inorganic backbone formed by alternating phosphorus and nitrogen atoms and with two side groups linked to the phosphorus atoms. Since Allcock and Kugel reported the preparation of some alkoxy substituting polyphosphazenes,[1] a variety of poly (organophosphazene)s (POPs) with different properties and applications,[2,3] such as nonlinear optical materials,[4,5] separation membrane materials[6,7] and biomaterials,[8,9] have been obtained through the substitution of poly(dichlorophosphazene) with organic groups. Considering their good film-forming ability and chemical structure tailoring property, polyphosphazenes are appropriate membrane materials. To improve the performance and resistance of polyphosphazene membranes, cross-linking technology has been often used.

Various cross-linking methods of POPs[10] has been reported, including free radical methodology,[6] ultraviolet (UV) radiation,[11,12] gamma irradiation,[13] and electron beam radiation.[14] Crosslinking by UV radiation can be conducted under ambient temperature, but for UV-opaque polyphosphazenes, such as aromatic containing polyphosphazenes, UV cannot penetrate into the deep area of membrane, leading to different cross-linking density in entire membrane.[13] Compared with UV radiation, the free radical methodology by heating can lead to uniform crosslinking of membrane.

The allyl groups were generally incorporated in POPs to facilitate free radical crosslinking process.[6,15] The conventional thermally cross-linking procedure was heating the polymer at minimum 110°C for minimum 10 min. However, it generally caused some unwanted thermally induced decomposition of POPs. Therefore, it can be expected that cross-linking at lower temperature may decrease decomposition of POPs and improves the durability of membrane to solvent. Other cross-linking conditions including oxygen and initiator also results in different swelling and solubility of POP membranes. In addition, the cross-linking mechanism of POPs with allyl groups was very complex and has not been studied in detail.

In this work, we focused on the study of thermally cross-linking of a polyorganophosphazene containing three substituents: phenoxy group, 2-allylphenoxy group, and ethoxy group (PAEPP). The influence of different cross-linking conditions, including time, temperature, and the amount of initiator, on the swelling degree and solubility of crosslinked PAEPP was discussed. The change of

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physical properties of membranes with different crosslinking conditions was clarified based on the analysis of the change of chemical structure. Further, cross-linking mechanism was proposed.

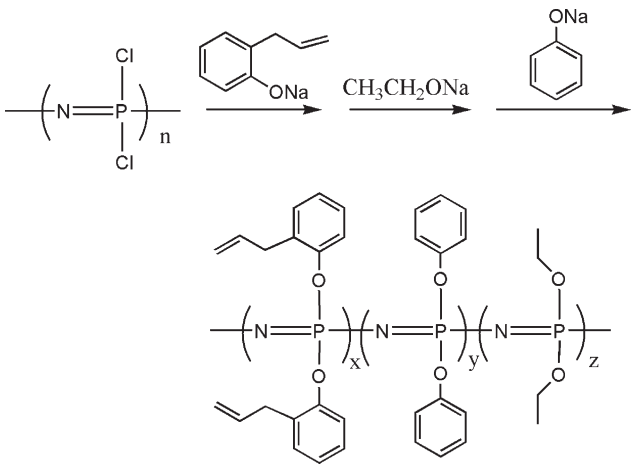
EXPERIMENTAL

Materials

Ethanol, petroleum ether, tetrabutylammonium bromide, azodiisobutyronitrile (AIBN), and phenol were purchased from Shanghai Chemical Reagents Corp. Sodium hydride (60% dispersion in mineral oil) was purchased from Rohm-Hass Corp. 2-allylphenol was purchased from Aldrich Corp. All of them were used without further purification. Tetrahydrofuran (THF, Shanghai Chemical Reagents Corp) was treated with sodium and was then distilled before used. Benzoyl peroxide (BPO, Shanghai Chemical Reagents Corp) was purified by several times of precipitation from THF solution to methanol.

Preparation of PAEPP

Poly(dichlorophosphazene) $(PNCl_2)_n$ was synthesized by one-step method as described by Carriedo et al.[16] The preparation route of PAEPP was shown in Scheme 1. The synthesis procedure was carried out as follows. $(PNCl_2)_n$ (4.46 g, 0.038 mol) and tetrabutylammonium bromide (0.10 g) were added to 50 mL THF in a 250 mL three-neck flask. Three solutions for substituting, i.e. the solutions of sodium 2-allylphenoxide, sodium ethoxide, and sodium phenoxide, were sequentially added to the $(PNCl_2)_n$ solution and stirred at 40°C, respectively, for 6, 24, and 24 h. The solution of 2-allylphenoxide was made via adding sodium hydride (0.246 g, 6.15 mmol) into the solution of 2-allylphenol (0.826 g, 6.72 mmol) with 50 mL of THF. The 2-allylphenoxide solution was stirred at room temperature until the sodium hydride was completely consumed, approximately in 5 min. The solution of ethoxide was prepared using ethanol (1.56 g, 0.034 mol) and sodium hydride (1.27 g, 0.032 mol) in 50 mL of THF. The resulting solution was stirred at 40°C for 10 min to ensure complete consumption of the sodium hydride. The solution of phenoxide was prepared using phenol (4.46 g, 0.048 mol) and sodium hydride (1.84 g, 0.046 mol) in 50 mL of THF. Isolation of the polymer was accomplished through precipitation into water and petroleum ether, respectively. The solid polymer was finally dried in vacuum. 2.42 g of a transparent brown elastomer was isolated in 48% yield.



Scheme 1 Preparation route of PAEPP.

Preparation and cross-linking of PAEPP membrane

PAEPP membranes were prepared using a solution casting method. Casting solutions were made from 3 mL THF with 0.12 g PAEPP and different contents of BPO (2, 4, 6, 8, and 10 wt.%). These solutions were stirred until all components were dissolved. The solutions were filtered to remove particulate matter and then poured on a PTFE plate (25 × 25 mm). The THF solvent was allowed to evaporate at room temperature to give yellow and transparent membranes. Cross-linking was carried out by heating the membrane in oven for predetermined temperature and time.

Analytical equipments and techniques

The ^1H NMR spectra were collected at 400 MHz on a Varian Mercury plus 400 spectrometer. ^{31}P NMR spectra at 162 MHz were obtained. The solvent used for NMR was D-chloroform. FTIR spectra were recorded on a Perkin–Elmer 936 spectrometer (Perkin–Elmer, USA) at room temperature. The general samples for FTIR characterization were prepared by following steps. One drop of the reaction mixture was placed on KBr plate (prepared from KBr powder) to form membrane. After that, the composite membranes were then placed in a controlled temperature oven for crosslinking reaction. Molecular weights were determined in DMF solution (1.5 mg/mL) by a Series 200 with a calibration curve for polystyrene standards. DSC analyses were performed on a PYRIS 1 DSC under a nitrogen atmosphere at a heating rate of 10°C/min (−60 °C to 80 °C). Before measured, the samples was washed with ethanol and dried under vaccum. Elemental analysis was conducted on PE 2400 (Perkin-Elmer).

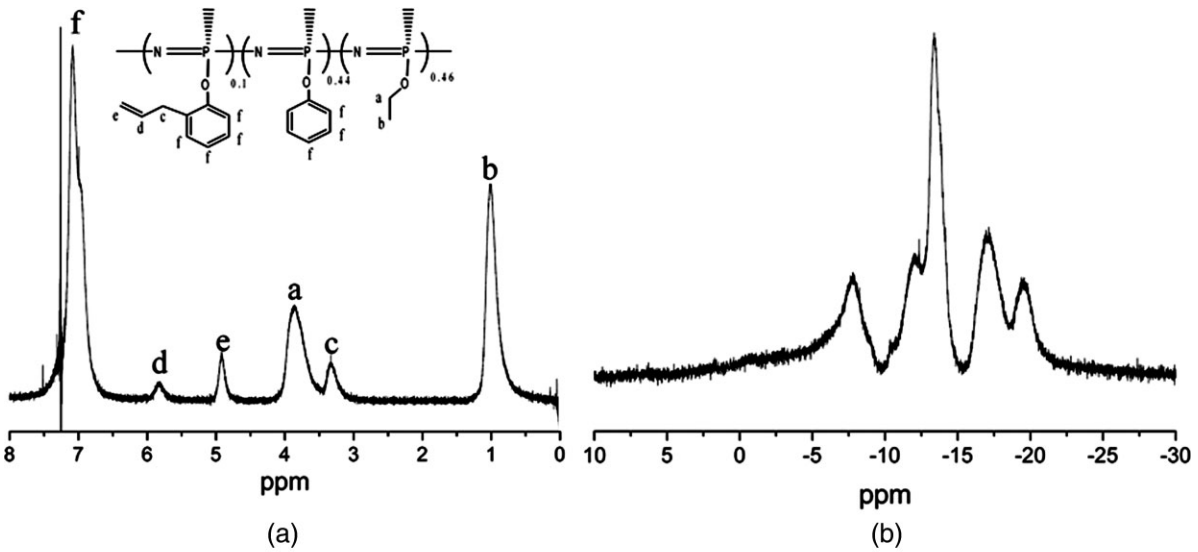


Figure 1 (a) ^{1}H NMR spectrum of PAEPP; (b) ^{31}P NMR spectrum of PAEPP.

Swelling and solubility determinations for thermally cross-linked PAEPP

Swelling and solubility of PAEPP were determined by immersing weighed portions of the differing polymers in THF at room temperature. After 1 day, the polymer samples were removed from solution, reweighed to gain the swollen weight. Then the swollen polymer was dried under vacuum for 24 h, and weighed to gain the dry weight of insoluble material that was used to calculate the degree of swelling. The solubility was calculated from the initial and final dry polymer weight.

$$\text{Swelling degree } [\%] = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

$$\text{Solubility } [\%] = \frac{W_o - W_d}{W_o} \times 100 \quad (2)$$

where W_o, W_d, and W_s are the weights of the original, dry, and swollen polymer samples. The values were obtained by three repeated experiments.

RESULTS AND DISCUSSION

Polymer characterization

^{1}H NMR spectrum of PAEPP and the assignment of peaks are shown in Figure 1a. The pendant group compositions are ethoxy 46%, 2-allylphenoxy 10%, and phenoxy 44%, which are obtained by integration of the ^{1}H NMR peaks. ^{31}P NMR spectrum of PAEPP, which is also provided in Figure 1b, shows five single broad peaks at −7.7, −12.1, −13.4, −17.1, and −19.6 ppm, respectively, assigned to the P atom substituted by two ethoxy groups, ethoxy and 2-allylphenoxy groups, ethoxy and phenoxy groups, 2-allylphenoxy and phenoxy groups and two phenoxy groups. The elemental analysis result is found: C, 54.2; N, 7.1; O 16.7; P 15.8; Cl 0.4 (Calcd: C 54.6; N 7.2; O 16.3; P 15.8; Cl 0). The number of chlorine is too small to affect the final property of crosslinked PAEPP. The molecular weight (M_n) of PAEPP is 132,000. DSC analysis of PAEPP shows that the glass transition temperature (T_g) is −34.3 °C and no melt peak occurs.

Characterization of crosslinked PAEPP

Chemical structure of polymers was analyzed by FTIR technique. FTIR spectra of PAEPP recorded before and after heating by 25 h at 85°C are shown in Figure 2a. Three following changes were observed after heating: (1) the broad carbonyl stretching band at 1651–1748 cm^{-1} occurs; (2) the C—O—O stretching band of peroxide at 1007 cm^{-1} increases[17]; (3) the band at 990 cm^{-1} assigned to vinyl species vanishes nearly completely.

In addition, the change of BPO (C=O at 1767 cm^{-1}), vinyl (C=C at 1641 cm^{-1}), ester (O=C—O—C at 1254 cm^{-1}), ether (C—O—C at 1196 cm^{-1}) and peroxide (C—O—O at 1007 cm^{-1}) were semi-quantitatively obtained by integration calculation which were, respectively, made for each FTIR spectrum for the regions of 1752–1777, 1628–1654, 1231–1309, 1177–1230, and 999–1014 cm^{-1}. The calculation equations are as follows:

$$A^0 = \frac{I^0}{I^0_{1600}} \quad (3)$$

$$A = \frac{I}{I_{1600}} \quad (4)$$

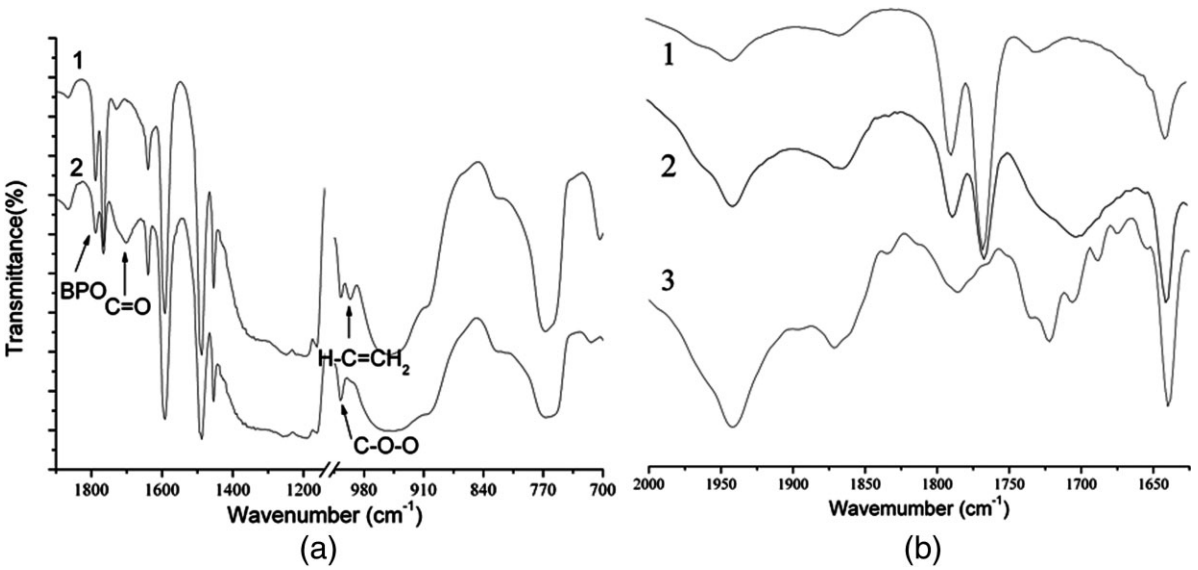


Figure 2 (a) FTIR spectra of PAEPP before 1) and after 2) heating at 85°C for 25 h; (b) FTIR spectra for region between 1625 and 2000 cm^{-1} of initial PAEPP (with BPO, 1), crosslinked PAEPP by heating at 85°C for 25 h (without washing with ethanol, 2) and crosslinked PAEPP by heating at 85°C for 25 h (washing with ethanol, 3).

$$\mathrm{Con_{BPO}} = \frac{A^0_{1767} - A_{1767}}{A^0_{1767}} \times 100\% \quad (5)$$

$$\mathrm{Con}_{vinyl} = \frac{A^0_{1641} - A_{1641}}{A^0_{1641}} \times 100\% \quad (6)$$

$$N_{\mathrm{ester}} = \frac{A_{1254} - A^0_{1254}}{A^0_{1254}} \times 100\% \quad (7)$$

$$N_{\mathrm{ether}} = \frac{A_{1196} - A^0_{1196}}{A^0_{1196}} \times 100\% \quad (8)$$

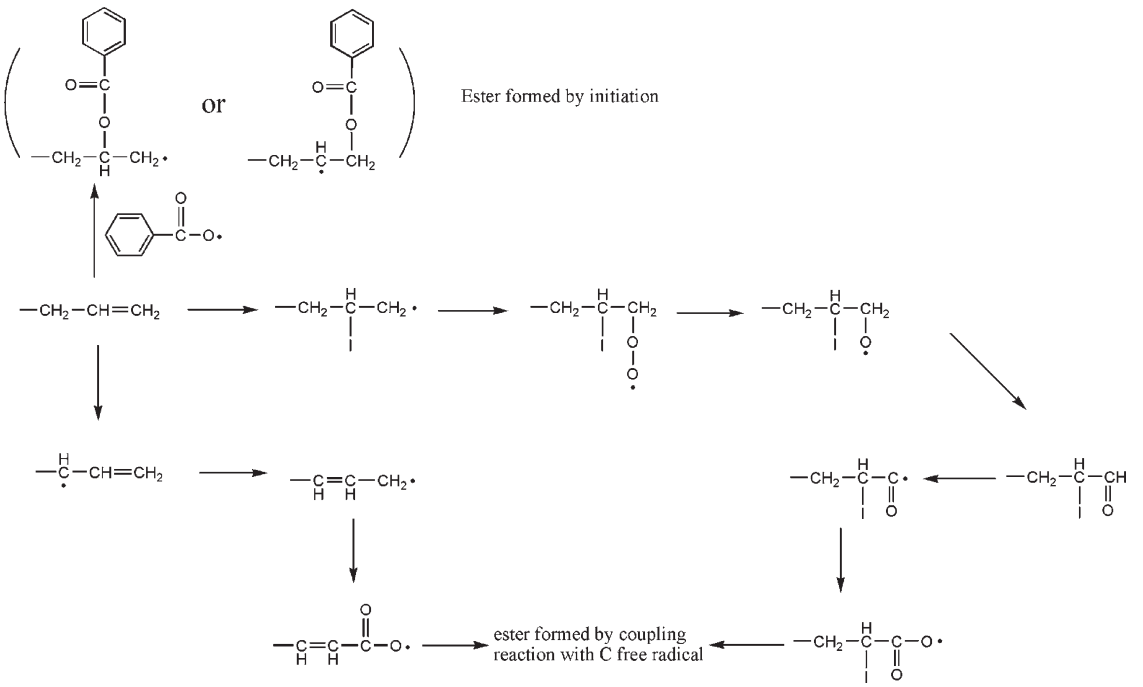
$$N_{\mathrm{peroxide}} = \frac{A_{1007} - A^0_{1007}}{A^0_{1007}} \times 100\% \quad (9)$$

where I^0 and I represent the intensity of studied band before and after crosslinking, I^0_{1600} and I_{1600} represent the intensity of benzene ring before and after crosslinking, A^0 and A represent the intensity ratio of studied band to benzene ring before and after crosslinking. For example, $A^0_{1767} = I^0_{1767}/I^0_{1600}$ and $A_{1767} = I_{1767}/I_{1600}$. $\mathrm{Con_{BPO}}$ and $\mathrm{Con_{vinyl}}$ represent the conversion ratio of BPO and vinyl. N_{peroxide}, N_{ether}, and N_{ester} represent the amount of peroxide, ether, and ester formed during crosslinking. The peak of benzene ring is set as the standard peak and all the data obtained from integration are used as relative areas. It is because the number of benzene ring remains the same after crosslinking reaction.

The calculated results are listed in Table I. The number of BPO decreases by 65%, which indicates decomposition of BPO to free radical initiators. The number of vinyl decreases by 32%, which shows the opening of double bonds by addition reaction. N_{peroxide}, N_{ether}, and N_{ester} are, respectively, 76%, 50%, and 80%, which indicates the formation of peroxide, ether, and ester. The formation of peroxide and ether bond is indicative of the presence of oxidization and the formation of macroradicals. The formation of ester band indicates the addition of benzoyl radical to carbon double bond. The ester was also formed by coupling reaction between O═C—O and C radical (Scheme 2).

TABLE I
Solubility, Swelling Degree, Conversion Ratio of Vinyl, Conversion Ratio of BPO, the Number of Peroxide and T_g of Crosslinked PAEPP with Time (at 85°C)

Time (h)	Solubility (%)	Swelling degree (%)	Conversion ratio of BPO (%)	Conversion ratio of vinyl (%)	The number of peroxidet (%)	T_g (°C)
0	100	–	0	0	0	−34.3
5	77.3	482	47	10.8	143	−32.0
10	38.5	478	60	18.4	115	−27.8
15	17.6	501	62	25.7	91	−23.1
20	5.1	440	64	32	66	−21.3
25	4.6	452	65	34	60	−21.0



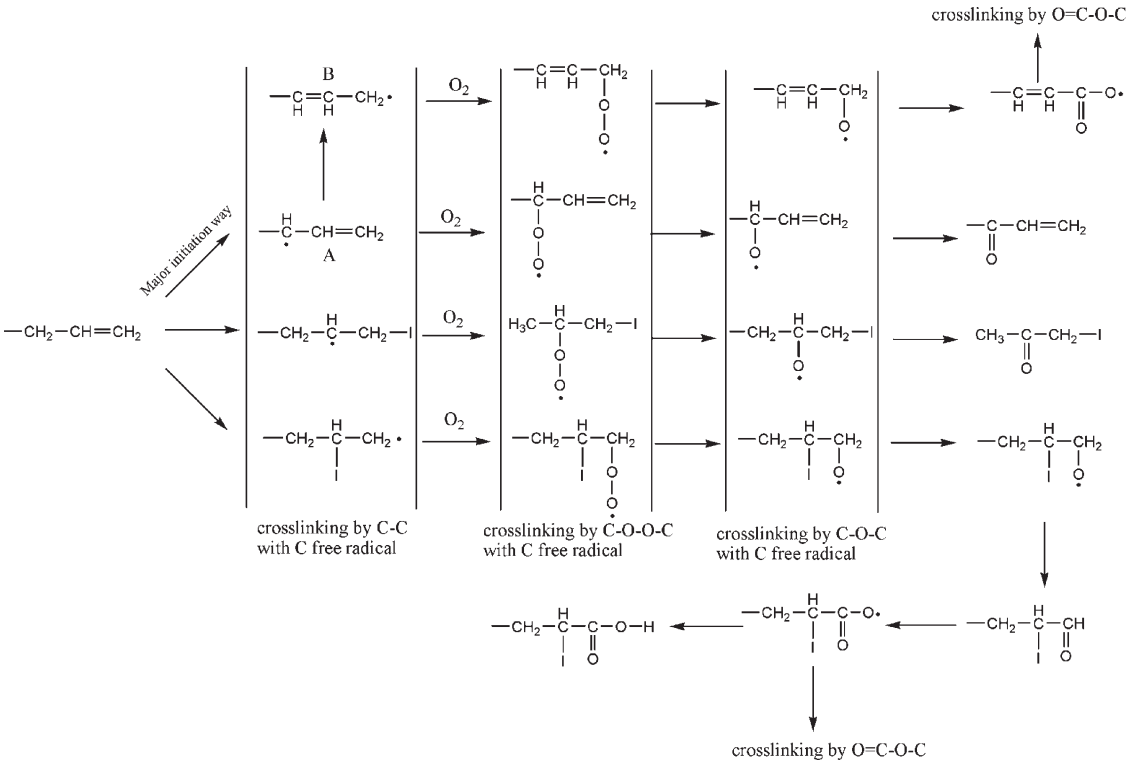
Scheme 2 The formation mechanism of ester during crosslinking.

The bands from 1651 to 1748 cm^{-1} correspond to carbonyl groups on polymer, benzoyl radical, and benzoic acid. The benzoyl radical and benzoic acid are the decomposition and derivative products of BPO. To verify the generation of carbonyl groups on polymer, the crosslinked PAEPP was washed with ethanol and the residual small molecules was removed. The preparation procedure of this sample for FTIR characterization was described as follows. The polymer solution was dropped on KBr plate to form a thin membrane. After crosslinking, this membrane was immersed in ethanol three times, each for 24 h. Finally, the membrane was dried in vacuum for 12 h. The FTIR spectra of uncrosslinked PAEPP (with BPO, spectrum 1), crosslinked PAEPP (with BPO, spectrum 2) and purified material (spectrum 3) for the region between 1625 and 2000 cm^{-1} are shown in Figure 2b for comparison. It can be found that the band from 1628 to 1654 cm^{-1} of BPO and some of bands in spectrum 3 from 1651 to 1748 cm^{-1} vanish, indicating that small molecules were removed. A series of characteristic bands of carbonyl group[18] are observed in spectrum 3, including bands at 1735 cm^{-1} and 1705 cm^{-1} assigned to ester, band at 1719 cm^{-1} assigned to carboxylic acid and bands at 1688, 1674, and 1654 cm^{-1} assigned to ketone and unsaturated carbonyl species. The presence of these bands supported the postulate that PAEPP was oxidized during crosslinking and different crosslinking sites were incorporated in PAEPP. Formation of ketone, carboxylic acid, and unsaturated carbonyl specie showed that free radicals took place on the three carbons on allyl group, which were all possible cross-linking sites (Scheme 3).

The effect of oxygen on crosslinking

In some previous reports,[19,20] it was reported that air facilitated grafting and cross-linking. In our experiments, it was suggested that oxidation effect took place in crosslinking procedure. Further, to clarify whether oxygen was necessary factor for crosslinking of PAEPP, the crosslinking was tried in nitrogen with BPO. The result showed that the obtained material was nearly completely dissolved in THF.

By integration calculation for FTIR spectra, it can be found that greatly larger number of crosslinking was formed in air. This was verified by comparing the increase ratios of the bands of ether (1196 cm^{-1}) and ester (1254 cm^{-1}) after crosslinking in air and nitrogen at 85°C for 25 h. For crosslinking in air, the values were, respectively, 50% and 80% which were greatly higher than the values obtained in nitrogen, respectively, 2% (the small amount ether formed in nitrogen was caused by a small amount of oxygen in polymer) and 23%. The results reported above clearly showed that the presence of oxygen greatly enhanced crosslinking of PAEPP. One reason was that oxygen enhanced the decomposition and initiation effect of BPO and the crosslinking. The higher conversion ratio of BPO in air (65%, at 85°C for 25 h) compared with that in nitrogen (only 40%) indicated a stronger initiation effect of BPO in air.



Scheme 3 The crosslinking mechanism of PAEPP.

Another reason was that the coupling reaction involving C—O and C—O—O free radicals was easier than the reaction between C free radicals. It was evidenced by the great number of peroxide formed in air.

The effect of time and temperature on crosslinking

Consistent with polymer network forming process,[21] with increasing heating time, the solubility of PAEPP decreased, the T_g of PAEPP increased (Table I) and the cross-linked PAEPP gradually became hard and fragile, which indicates that the cross-linking network of polymer increased. For crosslinking reaction at 85°C, 110°C, and 130°C, crosslinked materials were, respectively, formed at 5 h, 30 min, and 15 min. Almost no crosslinking was observed for PAEPP within 25 h at 60°C. Apparently, with increasing temperature, reaction rate increased.

Crosslinking process was always accompanied with chain scission. The competition between the two processes was investigated by solubility and swelling experiments. Solubility and swelling data for cross-linked PAEPP (6 wt.% BPO) with heating time at different temperatures are shown in Tables I and II. At 85°C, the solubility of PAEPP decreased with increasing curing time and kept the similar after 20 h. At 110°C and 130°C, the solubility of PAEPP decreased at early stage and increased with prolonged curing time. The increase of solubility was due to the decomposition of PAEPP. The soluble fraction of PAEPP cross-linked at 85°C was the lowest. The most likely explanation is that at 110°C and 130°C, the rate of thermally induced chain scission exceeds that of crosslinking, thus less complete cross-linking network was achieved as observed in the larger soluble fractions obtained. Swelling degree of all PAEPP membranes cross-linked with different time and temperature remained the similar level, except at relatively high temperature (110 and 130°C) when the reaction time exceeded 1 h, the swelling degree show an increase.

The change of solubility at 85°C can be explained by the corresponded transformation of chemical structure which was monitored by FTIR. From Table I, it can be seen that Con_{vinyl} and Con_{BPO} increases to about 32% and 65% gradually as the reaction is

TABLE II
Solubility and Swelling Degree of Cross-linked PAEPP Obtained at 110 and 130°C

	Temperature (110°C)		Temperature (130°C)	
Time (h)	Solubility (%)	Swelling degree (%)	Solubility (%)	Swelling degree (%)
0.5	23.4	527	65	463
1.0	14.8	476	39.4	463
1.5	34.1	703	72.5	625

TABLE III
Conversion Ratio of Vinyl and the Number of Peroxide of Crosslinked PAEPP with the Lowest Solubility at 85, 110, 130°C

Temperature (°C)	Conversion ratio of vinyl (%)	The number of peroxide (%)
85	34	143
110	60	192
130	86	240

carried out for 20 h. After that, the increase of Con_{vinyl} and Con_{BPO} greatly slows down. This change has the same trend with that of solubility and T_g. $N_{peroxide}$ increases by 143% as reaction is conducted for 5 h and further reaction otherwise leads to a decrease of $N_{peroxide}$. After 20 h, $N_{peroxide}$ almost does not change. The change of peroxides is determined by two process, including generation and consumption. The peroxides are generated by oxidization of C radicals. The consumption of peroxides is due to the transformation of C—O—O radicals to C—O radicals and other products derived from C—O radicals (Scheme 3). At first, the generation rate of C—O—O is faster than the decay rate of peroxides. It is because at this time, the concentration of initiator is high. However, with the reduction of initiator, the production rate of free radicals decreases but the decay rate of peroxides increases due to the increase of peroxides concentration. It results in a decrease of $N_{peroxide}$ until BPO does not decompose.

In Table III, Con_{vinyl} and $N_{peroxide}$ of crosslinked PAEPP with the lowest solubility at different temperature (85 °C, 110°C, and 130°C) are listed for the purpose of comparison. With increasing temperature, Con_{vinyl}, and $N_{peroxide}$ both increases. Theoretically, the solubility of crosslinked products should decrease. However, the solubility increases because higher temperature causes more serious degradation.

The effect of initiator on crosslinking

The crosslinking of PAEPP was tried without BPO in air at 85°C, 110°C, and 130°C. However, no obvious crosslinking was observed. It indicated that BPO was necessary for the crosslinking of PAEPP and of course, the initiation step was the necessary procedure to form crosslinked structure. In addition, in some reports,[6,15] 2 wt% BPO is enough to crosslink POPs and higher content of BPO has not been studied. In our study, we investigated the solubility of crosslinked PAEPP with different content of BPO at 85°C for 25 h. (Fig. 3). The solubility decreased as BPO content increased to 6% and after that, the solubility increased as BPO content increased from 6% to 10%. It was suggested that the most complete crosslinked network was formed with 6% BPO. Swelling degree of cross-linked PAEPP with different BPO concentration was similar, revealing the similar crosslinking density. The change trend of Con_{vinyl} and $N_{peroxide}$ with BPO content (Fig. 3) is consistent with that of solubility. Crosslinking with 6% BPO gave highest Con_{vinyl} and $N_{peroxide}$.

In some studies about chemical grafting,[22–24] this type of change trend was also reported. Based on their work, the results of our experiments could be explained by the following reasons: (1) the excessive BPO may act as a terminator of free radicals and decreases the rate of reaction; (2) during the course of crosslinking the flexibility of phosphazene chains decreased, which lowered the diffusion coefficient of BPO, especially for high concentration of BPO.[11]

Cross-linking mechanism

The cross-linking mechanism of PAEPP is proposed in Scheme 3. To investigate the role of addition reaction between carbon double bonds in the cross-linking mechanism of PAEPP initiated by BPO, in this study, we have tried another initiator AIBN which is well known for polymerization of vinyl material. Crosslinking with AIBN is done only by the addition between the double bond because AIBN could not abstract hydrogen atoms from polymer.[25,26] Experiments showed that no cross-linking of PAEPP initiated by AIBN took place in oxygen or nitrogen environment. The most likely explanation is resonance stabilization of the radical produced when AIBN dissociates. Another possible explanation is the relatively low reactivity of free radicals resulted form the initiation of carbon double bonds.

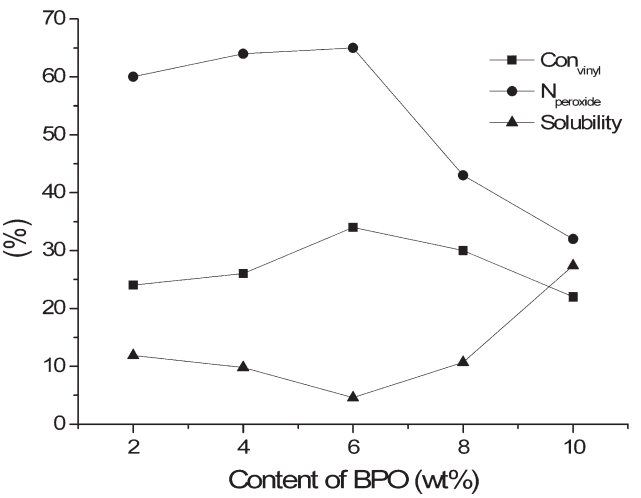


Figure 3 The effect of BPO content on the solubility of crosslinking PAEPP, conversion ratio of vinyl, conversion ratio of BPO, and the amount of peroxide by heating at 85°C.

As the crosslinking was initiated by BPO, the hydrogen atoms on methylene were abstracted to form allylic free radicals (A) which are evidenced by the unsaturated carbonyl group stretching band (Fig. 2b, spectrum 3). The free radicals A can transform to its isomer (B) (Scheme 3) with relatively low steric hindrance. Hence, the major reaction forming crosslinking is the most likely by addition of free radical B or its oxidization radicals to carbon double bond or coupling reaction between free radical B with another free radical or itself.

The linkage ways between polymer chains include alkyl, ether, peroxide, and ester bonds. The ether, peroxide, and ester bonds were verified by FTIR characterization. The alkyl bonds were inferred theoretically. Besides, the dominant cross-linking way to give cross-linked PAEPP[18] is ether, ester, and peroxide bonds. It can be explained that oxidation gives rise to different type of C—O—O and C—O free radicals that perhaps increases the activity of free radicals and facilitated crosslinking.

CONCLUSION

This work focused on the crosslinking of PAEPP initiated by BPO. After crosslinking, BPO decomposed, the amount of vinyl decreased, ester, and ether occurred and the amount of peroxide increased. Oxygen caused the oxidization reaction during crosslinking, increased the decomposition of BPO and enhanced crosslinking.

PAEPP was crosslinked in different conditions. The solubility of PAEPP and the number of vinyl and peroxide decreased with the crosslinking time. The solubility of PAEPP increased as the temperature increased owing to the decomposition of PAEPP. It was suggested that the crosslinking at 85°C is appropriate for PAEPP. With the increase of BPO amount, the conversion ratio of vinyl and BPO, the amount of peroxide and the solubility showed the same change trend—a maximum or minimum value was achieved with 6% BPO. Excessive BPO did not give low solubility of crosslinked PAEPP although it can increase reaction rate.

Initiation reaction preferentially took place at methylene producing allylic free radicals. Initiation or addition of vinyl also contributes to the crosslinking of PAEPP. The C free radicals resulted from initiation reaction were oxidized to form C—O—O and C—O free radicals. Forming ether and peroxide between polymer chains is the major crosslinking way for PAEPP.

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