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Mechanism of oxidative reaction in the post crosslinking of hypercrosslinked polymers

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Abstract

The post crosslinking reaction parameters were systematically studied for the investigation on formation mechanism of oxygen containing groups on the surface of hypercrosslinked polymers. The FT-IR spectra and the Boehm titration were employed to characterize the surface chemistry of the synthesized polymers. The GC-MS was used to analyze the nitrobenzene that was the solvent in the reaction. The functionalities for example carbonyls were formed through the oxidation of chloromethyl groups by nitrobenzene and the carboxylic groups were formed through further oxidation by oxygen during the synthesis process. Meanwhile the nitrobenzene was deoxidized to aniline.

Keywords: Post crosslinking; Oxidative reaction; Hypercrosslinked polymers; Nitrobenzene

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1. Instruction

Davankov and Tsyurupa described a new series of hypercrosslinked polymeric networks in 1969 [1–5]. It consists of making a large amount of rigid crosslinks between aromatic rings of linear polystyrene chains taken in swollen states. This yields hypercrosslinked polymers having a crosslinking degree of 100% and even higher.

Owing to their high internal surface area, unique porosity, and the excellent swelling feature, hypercrosslinked polymers have exhibited good adsorption affinities to a large number of organics and thus been extensively studied. The uses of these hypercrosslinked polymers for the adsorption of organic compounds such as phenols [6–8], synthetic organic dyes [9,10], *n*-valeric acid, lipids, tributyl phosphate and petroleum spirit [2] have been widely investigated. Streat and Sweetland [11] have studied the adsorption of organic pollutants for example phenols from potable water using hypercrosslinked polymers. Our group has also studied the adsorption of organic pollutants such as phenols [12–15], naphthalene derivatives [16], phenylhydrazine derivatives [17], lipoic acid [18] and phenylacetic acid [19] from wastewater by the hypercrosslinked polymers.

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Generally, the polymers crosslinked by polystyrenes possess an absolute hydrophobic surface and must be wetted by alcohol or acetone prior to use. However, it was recently found that the non-modified hypercrosslinked polystyrenes also could be partly hydrophilic, which is most likely due to the formation of oxygen containing groups involving phenolic, carbonyl and carboxylic groups on surfaces of the polymers. Streat and Sweetland [20] studied the complete physical and chemical properties of neutral hypercrosslinked polymer MN-200. It was proposed that the polar oxygen containing groups such as phenolic, carbonyl and carboxylic groups of the polymer was the result of hydrolysis of chloromethyl groups. Xu et al. [21] studied the side reaction of post crosslinking reactions during synthesis of hypercrosslinked polymers and it was put forward that carbonyl groups on the polymers were formed via oxidation of chloromethyl groups by oxygen in air.

Such functionalization or modification of polymer surfaces can significantly affect their adsorption properties toward heavy metals [22–26] and organic pollutants from aqueous solutions. So it is of great importance to investigate the formation mechanism of oxygen containing groups and to determine their nature and amount for application optimization of polymers.

In the present study, the synthesis parameters such as reaction carrier gas, temperature, solvent and water content of the raw materials were systematically studied to get hypercrosslinked polymers with different surface functional groups. FT-IR and Boehm titration were used to characterize the surface functional groups of the synthesized polymers. GC-MS was applied to analyze nitrobenzene that was the solvent during reaction process.

2. Experimental

2.1. Synthesis

The raw material for preparation of hypercrosslinked polymers was chloromethylated PS-DVB copolymer obtained from Langfang resin factory, China (original chlorine content: 19.5%). In a typical experiment, 50 g of the polymer was swollen overnight in 250 ml nitrobenzene. Some zinc chloride was added as catalyst to the reactor and the mixture was heated to a certain temperature and reacted for desired time. For evaluation of reaction process, samples of the reaction mixture were withdrawn from the reactor at selected time intervals during synthesis. Different reaction parameters such as reaction temperature (90 °C, 120 °C), solvent (nitrobenzene, dichlorobenzene), water content of raw material (0%, 5.4%) and reaction carrier gas (oxygen and nitrogen) were studied for the investigation of formation mechanism of oxygen containing groups. Then the polymer particles were filtered off, washed with ethanol, and extracted with ethanol in Soxhlet apparatus for 8 h. Finally the particles were washed in columns with dilute hydrochloric acid, ultralpure water and dilute sodium hydroxide repeatedly until there were no metal ions or other impurities. The polymers were converted to be hydrogen form before use.

2.2. Fourier transform infra red spectroscopy (FT-IR)

FT-IR spectra were recorded on a Nexus870 FT-IR spectrometer (Nicolet, USA). Before test the synthesized polymers were crushed to powder and mixed with finely divided spectroscopic grade potassium bromide. The background spectra of potassium bromide and water vapor were recorded every 100 min. Spectra were recorded at a resolution of 4 cm^{-1} using a minimum of 400 scans.

2.3. Boehm titration

Samples of polymers were contacted with 0.05 N solutions of sodium hydroxide, sodium hydrogen carbonate, sodium carbonate and sodium ethoxide [27]. Sodium ethoxide was dissolved in HPLC grade ethanol to prevent degradation caused by reaction with water. Dried polymers (0.5 g) were accurately weighed and then placed into 100 ml conical flasks prior to the addition of 25 ml of different bases. The flasks were sealed and stirred in an orbital shaker for 7 days. Each mixture was prepared in duplicate. Blank solution of each base was also stirred in the same conditions. After shaking 10 ml of the bases were put into a flask with 25 ml 0.05 N hydrochloric acid, then the mixture were titrated by 0.05 N standard solution of sodium hydroxide after 30 min using phenolphthalein as indicator.

2.4. Gas chromatography and mass spectrometry (GC-MS)

Mass identification was performed by a 6890 gas chromatography (Agilent, US) coupled to a GC-

TOF mass spectrometer (Micromass, UK). The ionization mode is EI (70). The column is 30 m × 0.25 m × 0.25 m and the column temperature keeps 70 °C for a minute and then rises from 70 °C to 250 °C at a rate of 10 °C/min.

3. Result and discussion

3.1. Fourier transform infra red spectroscopy (FT-IR)

Fig. 1 shows the FT-IR spectra obtained by the KB$_r$ pellet technique of the synthesized polymers at the 24th hour in nitrogen and oxygen respectively. The broad bands observed of the synthesized polymers in the range of 3500–3700 cm^{-1} can be assigned to O–H stretching vibrations in hydroxyl groups. The FT-IR spectrum of all the samples present the characteristic bands at 3017 cm^{-1} and 2925 cm^{-1} due to the symmetric and asymmetric C–H stretching vibrations indicating the presence of methylene groups [28]. The band at about 1700 cm^{-1} represents the strong stretching vibrations of the carbon oxygen double bond. The band at 1606 cm^{-1} appears in all the samples and can be assigned to aromatic ring stretching vibrations augmented by the presence of the carbon oxygen double bond conjugated with polymer basal planes, resulting in a stronger adsorption at 1606 cm^{-1}. The bands at 1510 cm^{-1} and 1451 cm^{-1} are also can be assigned to the aromatic ring stretching vibrations. The bands at about 1212 cm^{-1} and 1110 cm^{-1} in the FT-IR spectrum of the studied polymers can be assigned to C–O stretching vibrations in ether structures and hydroxyl groups respectively [29]. The bands at about 817 cm^{-1} and 703 cm^{-1} are suggested to be the C–H out of plane bending vibrations of the polymers basal plane. The bands at about 1266 cm^{-1} and 673 cm^{-1} represent the C–Cl stretching vibrations in chloromethyl groups.

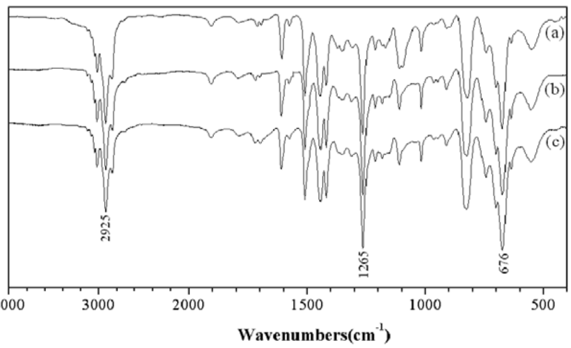

Fig. 2. IR spectra of the chloromethylated PS-DVB copolymers oxidized at 90 °C (a) and 120 °C (b) in air and the resin synthesized in dichlorobenzene (c).

Fig. 2 shows the FT-IR spectra of the chloromethylated PS-DVB copolymers oxidized at 90 °C and 120 °C in air. As shown in Fig. 2, the bands that can be assigned to the carbon oxygen double bond, ether structures and hydroxyl groups are absent in the spectra. There are only bands representing the symmetric and asymmetric C–H stretching vibrations of methylene groups, aromatic ring stretching vibrations and the C–Cl stretching vibrations in chloromethyl groups. It suggests that there are no oxygen containing groups on the surfaces of the oxidized raw materials in the air at 90 °C and 120 °C. So it is deduced that the formation of oxygen containing groups is not the result of oxidation of chloromethyl groups by oxygen. The FT-IR spectra of the polymers made from raw materials having different water content (0%, 5.4%) are also carried out and

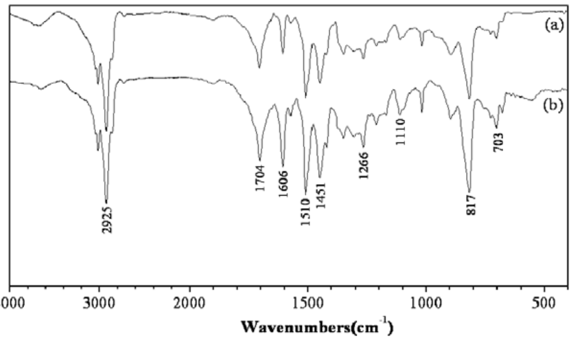

Fig. 1. IR spectra of the synthesized resins withdrawn at the 24th hour in nitrogen (a) and oxygen (b), respectively.

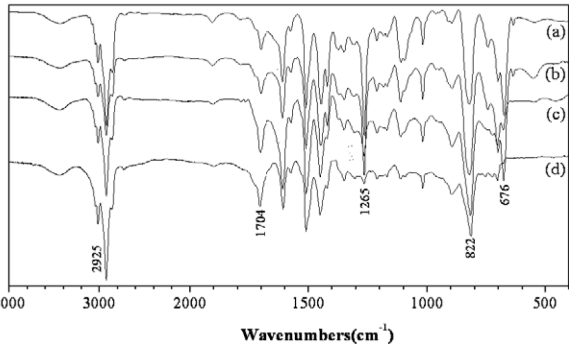

Fig. 3. IR spectra of the synthesized resins in nitrogen withdrawn at 2nd (a), 6th (b), 14th (c), 24th (d) hour, respectively.

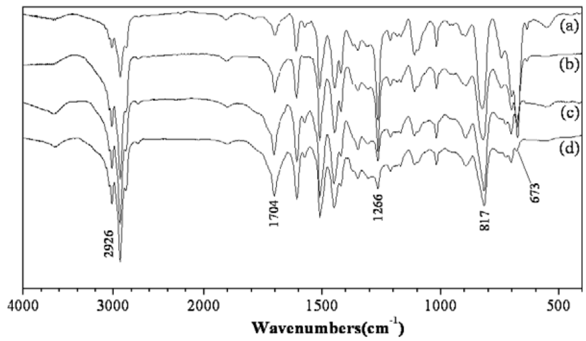

Fig. 4. IR spectra of the synthesized resins in oxygen withdrawn at 2nd (a), 6th (b), 14th (c), 24th (d) hour, respectively.

there are no differences between the two spectra. They both have oxygen containing groups indicating that the formation of oxygen containing groups are not the result of hydrolysis of chloromethyl groups.

As Figs. 3 and 4 show, the amount of the oxygen containing groups and the methylene groups increase with time in both nitrogen and oxygen and the increase slow down after the 14th hour. They also show that the chloromethyl groups of all the polymers decrease with the reaction time and the decrease slow down after the 14th hour. This indicates that the Friedle–Crafts reaction occurs at the studied conditions and the chloromethyl groups convert to methylene bridges. The chloromethyl group is more active at the beginning of post cross-linking reaction and the polymer network is more and more rigid which makes the conversion of chloromethyl groups to methylene bridges more difficult. At the same time the oxidation reaction also becomes difficult because of the inaccessible of the chloromethyl groups due to the rigidity of the polymer network. Then the conversion slows down. At the same time some of the chloromethyl groups are oxidized to oxygen containing groups during the reaction.

3.2. Boehm titration

The Boehm titration uses bases of different strength to differentiate between surface functionalities of various acid strengths. It is generally accepted that sodium hydrogen carbonate neutralizes only carboxyl groups on the polymers surface, sodium carbonate neutralizes carboxyls and lactones, sodium hydroxide neutralizes carboxyls, lactones and phenolic groups, sodium ethoxide neutralizes carboxyls, lactones, phenolic groups and carbonyls. According to the amount of different bases consumed we can calculate the amount of the oxygen containing groups.

The titration results of the polymers prepared in nitrogen withdrawn from the reactor at selected time intervals at different temperatures are shown in Table 1. The carbonyl and phenolic groups formed in the reaction and increased a little with time. It is also shown that more carbonyl and phenolic groups formed in higher temperature may be as the result of the more activity of chloromethyl group. Lactones only formed in higher temperature and changed a little with reaction time.

The titration results of polymers prepared in oxygen withdrawn from the reactor at selected time intervals at different temperatures are shown in Table 2. As Table 2 shows, in addition to the three kinds of groups present in Table 1 there are carboxylic groups in the polymers prepared in oxygen in higher temperature and it may form due to oxidation of other oxygen containing groups by oxygen. The three types of polar group in polymers prepared in oxygen mentioned above have the similar trend as

Table 1
Boehm titration results of resins prepared in nitrogen

		2 h	4 h	6 h	8 h	10 h	12 h	14 h	19 h	24 h
Carbonyls (mmol/g)	363 K	0.015	0.014	0.012	0.012	0.024	0.024	0.032	0.035	0.040
	378 K	0.028	0.026	0.024	0.036	0.036	0.036	0.036	0.048	0.058
	393 K	0.089	0.097	0.095	0.093	0.093	0.119	0.149	0.155	0.155
Phenols (mmol/g)	363 K	0.147	0.149	0.149	0.165	0.192	0.208	0.199	0.202	0.209
	378 K	0.167	0.158	0.171	0.177	0.173	0.208	0.220	0.203	0.213
	393 K	0.192	0.204	0.204	0.216	0.216	0.228	0.252	0.252	0.264
Lactones (mmol/g)	363 K	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	378 K	0.068	0.109	0.106	0.091	0.085	0.085	0.085	0.103	0.094
	393 K	0.039	0.039	0.051	0.057	0.059	0.065	0.062	0.071	0.083

N.D.: not detected.

Table 2
Boehm titration results of resins prepared in oxygen

		2 h	4 h	6 h	8 h	10 h	12 h	14 h	19 h	24 h
Carbonyls (mmol/g)	363 K	0.012	0.014	0.012	0.017	0.017	0.023	0.056	0.056	0.087
	378 K	0.05	0.07	0.07	0.07	0.140	0.105	0.140	0.140	0.140
	393 K	0.047	0.047	0.059	0.109	0.126	0.188	0.212	0.212	0.200
Phenols (mmol/g)	363 K	0.158	0.145	0.154	0.160	0.197	0.197	0.180	0.197	0.209
	378 K	0.178	0.178	0.185	0.185	0.192	0.192	0.201	0.201	0.219
	393 K	0.203	0.230	0.256	0.308	0.304	0.369	0.373	0.373	0.373
Lactones (mmol/g)	363 K	0.013	0.017	0.013	0.013	0.035	0.061	0.065	0.076	0.087
	378 K	0.035	0.066	0.078	0.083	0.083	0.078	0.078	0.083	0.083
	393 K	0.035	0.035	0.045	0.045	0.064	0.064	0.064	0.089	0.089
Carboxyls (mmol/g)	363 K	N.D.	N.D.	0.017	0.017	0.034	0.052	0.059	0.069	0.069
	378 K	0.018	0.018	0.035	0.035	0.035	0.053	0.070	0.053	0.088
	393 K	0.046	0.082	0.093	0.082	0.105	0.093	0.117	0.093	0.105

N.D.: not detected.

that in nitrogen. The more acidic groups such as carboxylic groups and lactones are absent in the polymers prepared at low temperature in the present study. We can see that all the titration results are consistent with results of the FT-IR spectra.

The titration experiments are also carried out to polymers synthesized in dichlorobenzene and the oxidized raw materials. The results show that there are no oxygen containing groups on the polymers tested and it is consistent with the FI-TR spectra. It suggests that the formation of functional groups may be induced by nitrobenzene and indicates the exception of oxidation mechanism of chloromethyl group by oxygen.

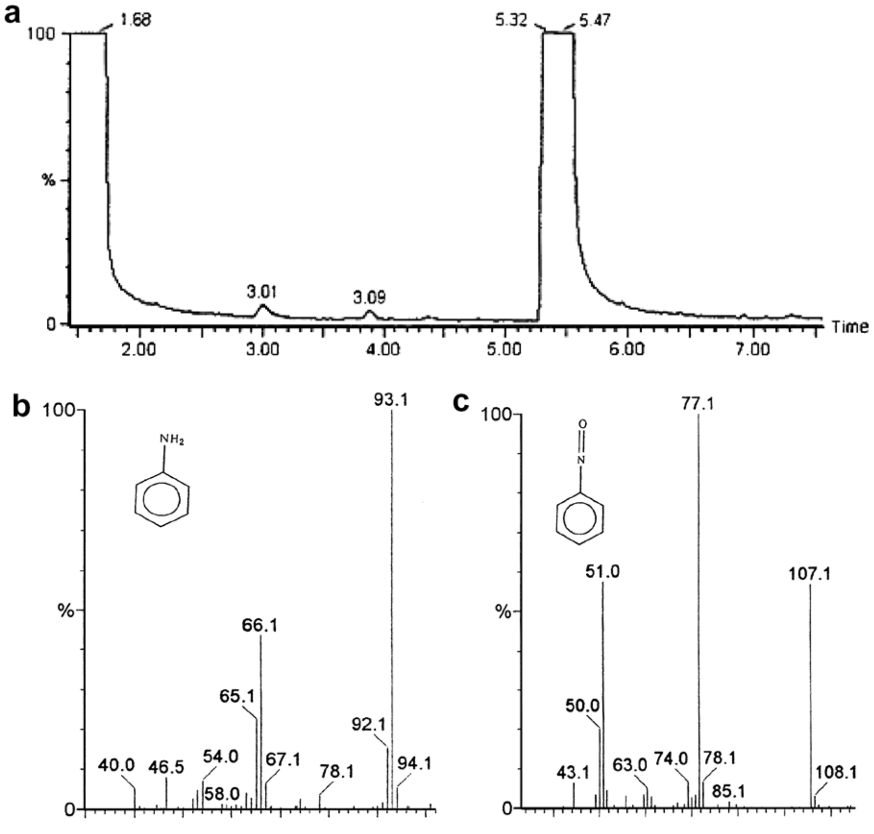

Fig. 5. GC-MS of nitrobenzene attending the reaction.

3.3. Formation mechanism of oxygen containing groups

The GC-MS analysis was carried out to nitrobenzene. Fig. 5 showed the GC-MS of nitrobenzene attending the reaction. In Fig. 5a, there were three important peaks. The peak appeared at 3.01 min and 3.09 min indicated respectively the existences of nitrosobenzene and aniline which were proved by the MS result showed in Fig. 5b and c. But nitrosobenzene and aniline were not detected in nitrobenzene that did not attend the reaction. This indicated that nitrobenzene is deoxidized to nitrosobenzene and further to aniline.

From the above analysis we can draw the conclusion that functional groups such as the carbonyls and the lactones are induced through oxidation of chloromethyl groups by nitrobenzene and the carboxylic groups may be formed by oxidation of the carbonyls by oxygen. The nitrobenzene was deoxidized to nitrosobenzene and further to aniline at the same time.

4. Conclusion

In this paper we systematically studied the reaction conditions to get polymers with different oxygen containing groups and further proposed the formation mechanism of these different groups. The FT-IR spectra and the Boehm titration were adopted to characterize surface chemistry of the synthesized polymers. According to the results it is concluded that the oxygen containing groups were neither formed through oxidation of chloromethyl groups by oxygen nor through hydrolysis of them. The functionalities for example carbonyls were formed through oxidation by nitrobenzene and the carboxylic groups were formed by further oxidation of carbonyls by oxygen. The nitrobenzene was deoxidized to aniline at the same time. The more detailed mechanisms should be studied in the further studies.

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