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Spontaneous gelation of poly(oligo-oxyethylene methacrylate)

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Summary

The spontaneous gelation of poly(oligo-oxyethylene methacrylate) was studied. When the solvent of the polymer solution was removed by freeze drying or evaporation under atmosphere, spontaneous gelation occurred. This gelation is caused by the radical generation and chain transfer reaction, which is evidenced by the prevention of gelation during freeze drying and evaporation under atmosphere with adding radical inhibitor into the polymer solution. The soluble residue of the crosslinked gel formed during freeze drying was found to be poly(ethylene glycol) which is the side chain of the polymer. This fact indicates that the cleavage of the side chain accompanies the gelation. The possible mechanism of the gelation is proposed with the idea that induced stress by solvent removal would cause the cleavage of the side chain and the generated radical is transferred to the other chain resulting in gelation.

Introduction

Poly(oligo-oxyethylene methacrylate)(poly(MEO_n)) is a comb-shaped polymer having the polymethacrylate backbone and poly(ethylene oxide) side chain which is attached to the backbone with ester linkage, and it is generally synthesized by radical polymerization of oligo-oxyethylene methacrylate ($CH_2{=}C(CH_3)COO(CH_2CH_2O)_nH$) macromonomer ($MEO_n$). Due to high salt-solvating power, low glass transition temperature and low crystallinity of poly(MEO_n), a special attention has been made to its application for solid polymer electrolyte. Many studies were devoted to homopolymerization (1,4), copolymerization (2,5~8) and electrical properties of its salt complex as a solid polymer electrolyte (1,4~8). In their works, however, it was sometimes reported that poly(MEO_n)s were spontaneously crosslinked to form a gel during polymerization, purification and drying procedures. D. J. Bannister et. al. (1) reported that the crosslinked product which swelled but did not completely dissolve in water was obtained when the acetone was evaporated from the acetone solution of the poly(MEO_n). H. Ohno and his coworkers (7) also reported that gelation through solution polymerization of poly(MEO_7) occurred when it was kept as relatively concentrated THF solution above 0.5 mol/*l* at 60°C and that solution polymerization under vacuum also

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caused gelation at even less than 0.2 mol/*l*. F. Yan et al. (3) observed the spontaneous gelation during polymerization, purification or after some months of conversion at room temperature. G. Bo et al. (2) studied the gelation during the copolymerization of MEO_n and methacrylate and acrylate in toluene. In that study they found that the gelation during polymerization was attributed to the chain transfer reaction. However, the detailed and intensive investigation on the gelation during purification and drying was not performed in their work, though such phenomena had been frequently reported. It was proposed that the reaction of poly(MEO_n) with silica (1) or oxygen (4) would cause gelation, but no experimental evidences were given. Due to such uncontrolled gelations, there was a difficulty in preparation of the solid polymer electrolyte film with desired salt content and film thickness.

In this work, we investigated the characteristics of the gelation behavior and tried to find the conditions of the spontaneous gelation and also discussed the possible mechanism. We concentrated our study on the gelation of poly(MEO_9) during solvent removal as in freeze drying or evaporation of the cast under atmosphere.

Experimental

Preparation of Materials

The oligo-oxyethylene methacrylate (MEO_9) was used as supplied by Aldrich. The polymerization of MEO_9 was carried out for more than 12hrs in water medium using redox initiator ($K_2S_2O_8$, $NaHSO_3$). In each run, the monomer concentration, amount of initiator and reaction temperature were changed in order to find the conditions at which gelation occurred during polymerization. The composition of reaction mixture and polymerization temperature are given in Table 1. After polymerization, unreacted monomer was removed by extraction using diethyl ether.

Freeze Drying

Freeze drying was carried out using Labconco freeze dryer. The shell freezing temperature was -50°C and the pressure of the vacuum chamber was about 200μmHg.

^1H and ^{13}C NMR Measurement

The ^1H NMR spectra and proton decoupled ^{13}C NMR spectra were recorded on Bruker AMX 500 (Field strength: 500MHz). The solvent used for the sample preparation was D_2O. Hexamethylenedisiloxane was used as a reference (0 ppm for ^1H NMR spectra and 2.03 ppm for ^{13}C NMR spectra).

Results and discussion

The effect of the polymerization condition on the gelation of poly(MEO_9) is given in Table 1. Gelation during the polymerization occurred when the concentration of monomer and the reaction temperature were relatively high. For the run number 4 and 5, the solutions appeared to reach a gel state about two hours and one hour after the addition of initiator respectively. These results support the conclusion drawn by G. Bo and his coworkers (2). They stated that the chain transfer and coupling of the radicals cause the gelation of poly(MEO_n) and the formation of soluble polymer is favored by high dilution of the reaction mixture and the presence of chain transfer agents. High monomer concentration and high reaction temperature lead to high probability of chain transfer and coupling reaction due to the high radical concentration, which results in gelation.

For the homogeneous polymer solution obtained from the run 3, gelation during drying procedure was investigated. The unreacted monomer was removed from the resulting polymer solution by extraction with diethyl ether in which only the monomer could dissolve. The amount of unreacted monomer was 5% by the weight of the feed. Therefore, the polymer concentration of the purified solution was about 4.75wt%. The ^{13}C NMR spectrum of the polymer solution is shown in Fig. 1(a). The peaks corresponding to the carbons in side chain are shown in 60~80 ppm. The chemical shifts of the methylene carbon, quaternary carbon and α-methyl carbon are corresponding to the 47, 41 and 22 ppm respectively.

Table 1. Effect of polymerization condition on gelation during reaction

Run number	wt. of oligo-oxyethylene methacrylate	Monomer concentration	wt. of initiator ($K_2S_2O_8$/$NaHSO_3$)	Reaction Temp. (°C)	Comment
1	5g	2.5wt%	37.5/15(mg/mg)	25	no gelation
2	5g	5.0wt%	37.5/15(mg/mg)	30	no gelation
3	5g	5.0wt%	50/20(mg/mg)	30	no gelation
4	5g	5.0wt%	37.5/15(mg/mg)	40	gelation
5	5g	8.0wt%	50/20(mg/mg)	40	gelation

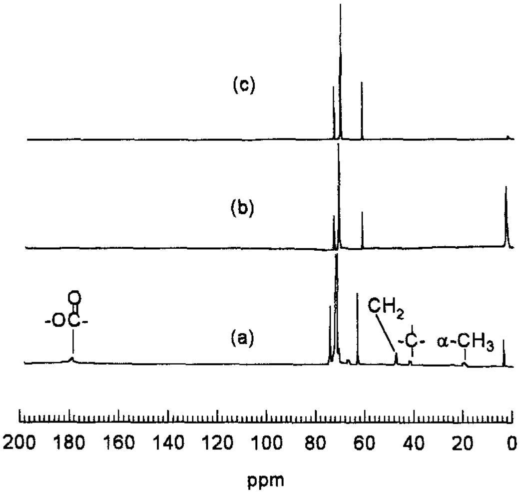

Fig. 1 ^{13}C NMR spectra of
a) uncrosslinked poly(oligo-oxyethylene methacrylate)
b) soluble residue of freeze dried poly(oligo-oxyethylene methacrylate)
c) polyethylene glycol of which molecular weight is 400.

Some parts of the aqueous polymer solution were kept in a closed glass bottle or polyethylene bottle at room temperature for more than 4 months. For both cases, no spontaneous gelation occurred. When these closed bottles were heated and maintained at 40°C for 24hrs, gelation did not occur. It seems that the poly(MEO_9) is stable in solution state of which concentration is 4.75wt%. In our investigations, spontaneous gelation was observed when the solvent was removed by freeze drying or evaporation under atmosphere. Especially freeze drying was found to be a very effective procedure for obtaining the crosslinked gel. The effect of the drying condition on the gelation is summarized in Table 2.

Table 2. Effect of drying condition on gelation

Procedure	Physical State
Preserving the polymer solution in a closed glass bottle at room temperature for more than 4 months	no gelation (viscous liquid)
Preserving the polymer solution in a closed polyethylene bottle at room temperature for more than 4 months	no gelation (viscous liquid)
Preserving the polymer solution in a closed glass bottle at 40°C for 24 hrs	no gelation (viscous liquid)
Preserving the polymer solution in a closed polyethylene bottle at 40°C for 24 hrs	no gelation (viscous liquid)
Freeze drying in a glass bottle without inhibitor	gelation
Freeze drying in a polyethylene bottle without inhibitor	gelation
Freeze drying in a glass bottle without inhibitor wrapped with aluminum foil	gelation
Freeze drying in a glass bottle with 2000 ppm hydroquinone	slight gelation
Freeze drying in a glass bottle with 9000 ppm hydroquinone	no gelation (highly viscous liquid)
Evaporation under atmosphere at room temperature without inhibitor	slight gelation
Evaporation under atmosphere at room temperature with 2000 ppm hydroquinone	no gelation (highly viscous liquid)
Evaporation under atmosphere at room temperature with 9000 ppm hydroquinone	no gelation (highly viscous liquid)

To confirm that the gelation during the drying procedures is due to radical generation, hydroquinone as a radical inhibitor was added to the polymer solution. For the stabilized solution with 9000 ppm hydroquinone, no gelation was observed during both the freeze drying and the evaporation under atmosphere, while for the solution containing 2000 ppm hydroquinone, slight gelation was found during freeze drying and no gelation was observed during evaporation under atmosphere. These facts evidently show that the gelation is caused by the radical generation and the consequent chain transfer reaction as is for the gelation during the polymerization.

D. J. Bannister et. al. (1) commented that the silica might crosslink poly(MEO_n). In order to evaluate this consideration, the polymer solutions without inhibitor were freeze-dried in a glass bottle or in a polyethylene bottle. The gelation was observed for both cases, indicating that silica does not play a major role in gelation. It was reported that the oligo-oxyethylene methacrylate is polymerizable by UV (9). However, the gelation also occurred during freeze drying when the bottle was wrapped with aluminum foil to prevent the access of light, which shows that the radical was not generated by UV.

The gelation always occurred when the solvent was removed by evaporation or freeze drying without inhibitor as shown in Table. 2. This fact represents that the radical generation is associated with the solvent removal. Radical generation is not due to the chemical reaction with solvent as evidenced by the absence of gelation when the solution was kept in a closed bottle for more than 4 months. Radical generation by mechanical stress induced by solvent removal is more feasible than by chemical reaction. When the solvent is removed from the polymer solution during the freeze drying or evaporation under atmosphere, the phase transition of the solvent could generate local stress, and it could result in chain cleavage if the induced stress was not fully dissipated by molecular motion of chain. This consideration gives rise to the question that why gelation does not occur for poly(methyl methacrylate) during the freeze drying. Though the poly(methyl methacryalte) and poly(MEO_n) have similar backbone structure, the length of the side substituent is quite different. For poly(MEO_n), a side chain could be easily entangled with each other due to the proximity of the neighboring side chain. When the solution is frozen or fully concentrated, the induced local stress would be dissipated by cleavage of side chain rather than by molecular motion accompanying disentangle of the side chain. It is very interesting to note that the copolymer of oligo-oxyethylene methacrylate and methyl methacrylate shows the spontaneous gelation during freeze drying only when the copolymer composition of the oligo-oxyethylene methacrylate unit exceeds about 35mol% (10). It suggests that entanglement of neighboring side chain is closely related to the gelation.

The crosslinked gels prepared by freeze drying and evaporation under atmosphere were not completely dissolved in water. The soluble residue of the freeze dried sample was extracted by immersing the crosslinked sample into D_2O. The ^{13}C NMR spectra of the filtered D_2O solution containing soluble residue is given in Fig. 1(b). Compared to the spectra of uncrosslinked poly(MEO_9), the peaks corresponding to the carbonyl carbon in ester linkage, α-methyl carbon and quaternary carbon in methacrylate backbone are absent and the peaks corresponding to the carbons in only the side chain are found. This spectrum is exactly consistent with that of PEG 400 as given in Fig. 1(c). This result clearly shows that the cleavage of side chain accompanies the gelation and it also confirms the idea that the induced stress during solvent evaporation is dissipated by the cleavage of side chain. The site at which bond scission occurs can be determined by means of ^1H NMR spectroscopy. In case that the scission of the oxygen in the ester group occurs, the ratio of the intensity of the methylene proton adjacent to OH end group (δ=3.63) and the remainder of the methylene protons in the internal EO units (δ=3.69) should be 1:8. The observed value for soluble residue was 1: 8.54 which is comparable to the value of 8. This results clearly indicates that the bond scission at the oxygen in the ester group occurs during the gelation. The gelation mechanism that satisfies the above NMR results is suggested as given in Fig. 2.

In this mechanism, the generated radical in the backbone is transferred to the proton in another chain and coupling reaction produces the soluble residue. Though the generated radical by chain cleavage is described, in Fig. 2, to be transferred to the proton in methylene unit in the main chain, it is also possible that the radical is transferred to the other protons such as the protons in the side chain. The evolution of carbon monoxide in the crosslinking reaction is suggested based on the information that the carbonyl radicals are frequently decomposed into carbon monoxide and alkyl or aromatic radical (10,11). Additionally, it should be stressed that the gelation occurred more significantly during freeze drying than during evaporation under atmosphere. The more significant gelation in freeze drying would be due to the higher stress induced by higher evaporation rate and to the lower dissipation through local molecular motion which is significantly reduced in frozen state. It is worth to note that the polymer should be kept in dilute solution and fast solvent removal as in freeze drying be avoided to prevent spontaneous gelation.

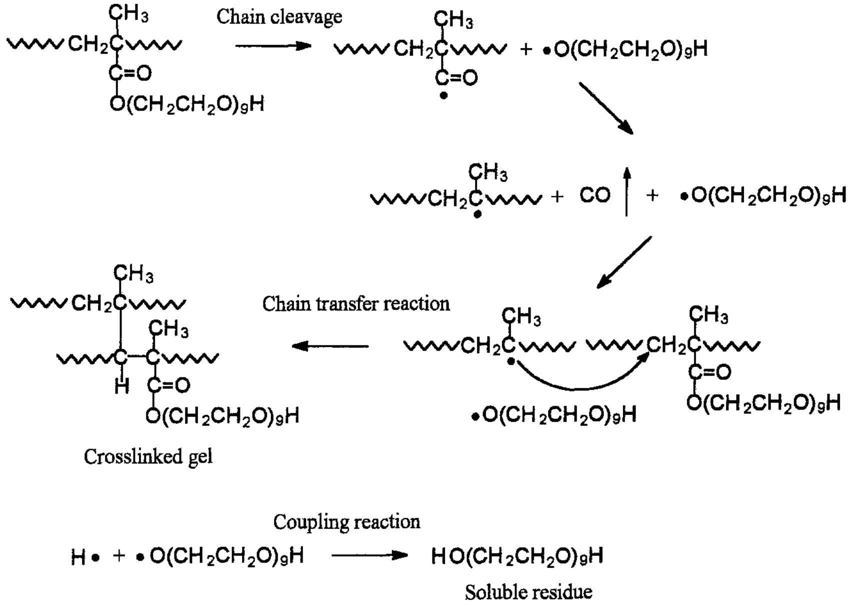

Fig. 2 Schematic representation of gelation mechanism

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