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THE POLYMERIZATION OF ACRYLAMIDE IN THE PRESENCE OF POLY(ETHYLENE GLYCOL)—II

ARUN V. PANTAR
Department of Chemistry, University of Delhi, Delhi 110007, India

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Abstract—Polymerization of acrylamide was studied in the presence of poly(ethylene glycol)s 200 and 400 (PEG) in two diluents, viz. water and methanol, using ammonium persulphate as radical initiator. The polymers prepared in methanol, in general, were of lower intrinsic viscosity than those obtained from an aqueous medium. All the polymers occluded PEG, resulting in a substantial improvement in solubility of polyacrylamide. The extent of occlusion depends on the initial concentrations of PEG in the reaction mixture. NMR and i.r. of the polymers reveal that some molecules of PEG or segments of PEG chains are closely bound to the polyacrylamide backbone. No significant changes in thermal properties were found.

INTRODUCTION

Polymerization of acrylamide (AAm) using the redox couple ammonium persulphate and tetramethylethylenediamine (TEMED) in the presence of poly(ethylene glycol)-200 (PEG-200) and -1500, using methanol as diluent has been reported [1]. It was observed that PEG was occluded in the polyacrylamide (PAAm) matrix, leading to a substantial improvement in the solubility characteristics of PAAm. This was also true when AAm polymerization was initiated by liquid oligoethyleneglycols [2]. The results of an investigation on persulphate initiated polymerization of acrylamide (AAm) in the presence of PEG using methanol or water as diluent are reported here.

MATERIALS AND METHODS

AAm (BDH) was recrystallized from benzene. PEG-200, and -400 (Sigma) were dried before use over P_4O_{10}. The initiator ammonium persulphate (S. Merck) was of GR quality. *N,N,N′,N″*-tetramethylethylenediamine (TEMED) was obtained from Sigma. Methanol was distilled and dried before use.

Table 1. Polymerization of acrylamide (AAm) in the presence of poly(ethylene glycol) (PEG) in methanol or water. Temperature: 35 ± 0.1°C; methanol/water, 2.5 ml; PEG-200/400, 2.8 g; ammonium persulphate, 1% (w/v): 0.1 ml; tetramethylethylenediamine (TEMED), 23% (v/v): 0.1 ml

	AAm (g)	M/I* $\times 10^{-3}$	ml g^{-1}
PP200-1†	1.0	1.4	51.9
PP200-2	2.0	2.9	60.0
PP200-3	4.0	5.9	86.2
PP200-4	5.0	7.4	89.4
PP400-1†	1.0	1.4	91.2
PP400-2	2.0	2.9	129.3
PP400-3	4.0	5.9	185.0
PPW200-1‡	1.0	1.4	45.8
PPW200-2	3.0	4.4	173.5
PPW200-3	4.0	5.9	203.4

*Monomer to initiator ratio.
†Polymerization in methanol medium.
‡Polymerization medium: water.

AAm was added to a mixture of methanol/water (2.5 ml) and PEG-200/400 (2.8 g), and stirred on a mixer until all the AAm dissolved. Details of the polymerization parameters are given in Table 1. In all the preparations, the amount of PEG was kept constant but the amount of AAm was varied. The polymerization mixture was maintained at 35°C for about 20 min, then TEMED followed by ammonium persulphate was added. The polymerization was allowed to proceed for 40 hr in systems containing methanol and for 5 hr in aqueous systems. The solid polymers were filtered, washed thoroughly with dry methanol and then dried in vacuum over P_4O_{10}. Polymers prepared in the presence of PEG-200/PEG-400 and in methanol are designated as PP200-X and PP400-X, and those in PEG-200 and water as PPW200-X.

Intrinsic viscosities of the polymers were determined in water at 30 ± 1°C using an Ubbelhode dilution viscometer. i.r. Spectra of the polymers were recorded with a Perkin-Elmer 621 unit. Films formed on 'parafilm' substrate from aqueous solution were peeled off and used for i.r. spectra. NMR spectra of polymers dissolved in D_2O (10%, w/v) and taken in a 5 mm tube were recorded with a Perkin-Elmer 90 MHz unit; tetramethylsilane was taken as external reference and the probe temperature was 40°C.

Weight loss of polymers with increasing temperature was determined with a Setaram unit, for a heating rate of $10°C\,min^{-1}$.

Dissolution rate studies were carried out by synthetic boundary experiments in a double sector cell in a Beckman Model-E Analytical Ultracentrifuge at 25°C.

RESULTS AND DISCUSSION

The contents of the polymerization mixture and the data for the resulting polymers are shown in Table 1. Polymerization of AAm in methanol in the presence of PEG is slow (30–36 hr); in aqueous medium it was rapid (4–5 hr) and occurs with liberation of heat and even explosive sounds (PPW200-2 and 3).

Polymers PP200-X and PP400-X obtained in methanol were free flowing powders. The polymers formed in aqueous medium were translucent and soft gels; on washing with methanol, they turned into hard milky white lumps akin to those reported [3] for pure polyacrylamide. All the polymers were hygroscopic and were stored in vacuum over a desiccant. The PPW200-X polymers were powdered by first placing the larger lumps in liquid N_2 and then grinding in an agate mortar.

The intrinsic viscosities of the polymers in the three series PP200-X, PP400-X and PPW200-X, increased with increase in M/I but irregularly (Table 1). Intrinsic viscosities of polymers obtained in methanol are generally less than those from the aqueous system.

Methanol, being a good chain transfer agent for acrylamide [4], is expected to reduce the chain size, but the presence of PEG decreases chain transfer and moderate chain size resulted. However, the intrinsic viscosity of PPW200-1, the polymer obtained in aqueous medium, is the least for all the three systems.

i.r. Studies

The i.r. spectra of the polymers in the region 1000–1200 and 1550–1700 cm^{-1} are depicted in Fig. 1. PEG-200/400 has a characteristic intense band [5] at 1102 cm^{-1} due to CO/CC stretching vibrations. Characteristic bands [3] for PAAm appear at 1660 cm^{-1} due to the CO stretching of amide carbonyl, which is well separated from the 1615 cm^{-1} NH_2 twisting vibration.

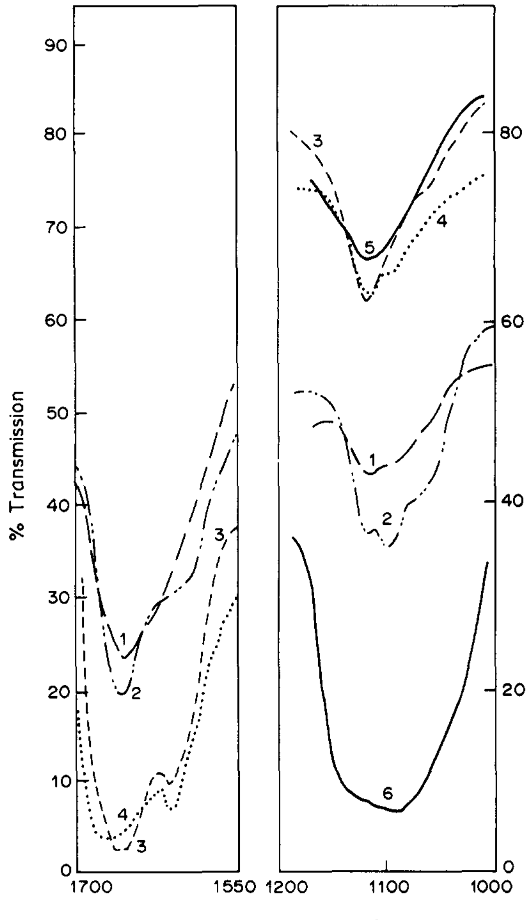

Fig. 1. i.r. Spectra of PP200-4 (1), PP200-1 (2), PP200-4 reprecipitated (3). PP200-1 reprecipitated (4), PAAm (5) and PEG-200 (6).

In all the polymers reported here, the 1102 cm^{-1} band is clearly seen indicating the presence of PEG; further the 1660 and 1615 cm^{-1} bands of PAAm have apparently merged to give a single broad band (Fig. 1). The occurrence of this feature is shown to be due to the presence of PEG in the following manner. A dilute aqueous solution of these polymers was "reprecipitated" by methanol and the resulting polymer showed considerable decrease in the intensity of the 1102 cm^{-1} band, with reappearance of delineated 1660 and 1615 cm^{-1} bands of PAAm [Fig. 1 (3) and (4)]. This observation clearly implies that PEG is washed out by "precipitating" so that it was merely occluded in the PAAm matrix and its removal set free the twisting motion of the side chain amide NH_2. This feature is also confirmed from NMR studies. It can be noted here that PEG occluded in PAAm cannot be removed by extensive washing with methanol after completion of polymerizations.

NMR studies

NMR spectra of the polymers recorded in D_2O are depicted in Fig. 2. The incorporation of PEG in the polymers is shown by the characteristic resonance at 3.65δ due to (CH_2CH_2O) protons [6]. Significantly, a peak is present in all the polymers at 3.65δ, and this peak splits into a doublet in high intrinsic viscosity systems (Fig. 2). This feature is discussed below.

Protons of the backbone of PAAm have resonance peaks [7] at 1.7 and 2.2δ. The ratio of PEG to AAm residues in the polymer samples was estimated from the relative areas under the PEG peak and PAAm backbone peaks.

The extent of PEG incorporated into the polymers is, as can be seen from Fig. 3, a function of its

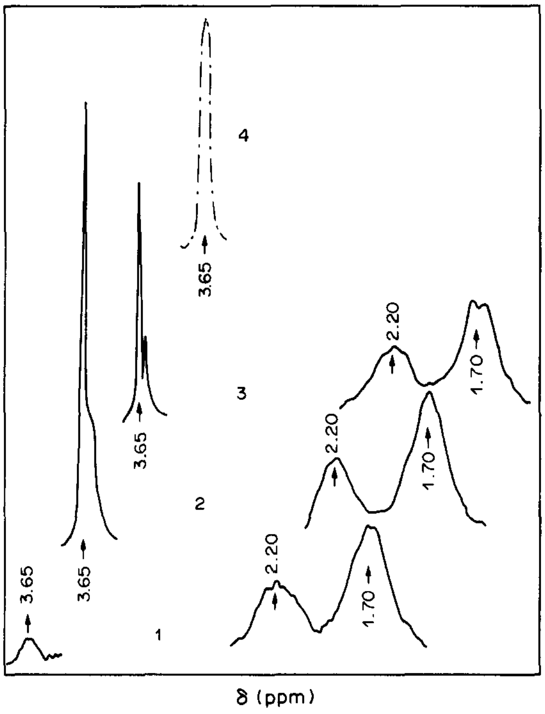

Fig. 2. NMR spectra of PP200-1 (1), PP200-4 (2), PP200-4 reprecipitated (3) and PEG-200 (4).

concentration in the reaction mixture. The polymers obtained in the aqueous medium apparently abstract a large amount (almost all) of PEG as compared to methanol medium. This can occur because water is a solvent for PAAm and is expected to solvate the polymer chain resulting in an expansion of the polymer matrix so that it can "occlude" more PEG. Methanol being a non-solvent enhances polymer chain interactions in PAAm and thus compact PAAm polymers largely free from PEG are obtained. However, PEG molecules closely associated with the monomer AAm became incorporated during polymerization in the PAAm matrix. This also explains the powdery nature of these polymers.

The NMR spectra of "reprecipitated" polymers had considerably reduced 3.65δ peak indicating almost complete loss of PEG (Fig. 2).

An indication of the unequal doublet at 3.65δ $\leftarrow CH_2CH_2O \rightarrow$ peak, taken in conjunction with i.r. observation, reveals that the ethereal oxygen atoms of PEG are involved in extensive hydrogen bonding with the NH_2 of the amide in PAAm. Due to this hydrogen bonding, certain PEG molecules or regions of the PEG chain are contained in a compact PAAm environment resulting in the differentiation in magnetic behaviour of these ethylene protons. For this reason, i.r. spectra of PEG containing PAAm did not show a clear band for NH_2 twisting.

Similar features are also observed for PPW200-X polymers but the 3.65δ $\leftarrow CH_2CH_2O \rightarrow$ peak in NMR and 1102 cm^{-1} CO/CC stretching vibration were strong and broad.

Thermogravimetry

The continuous weight loss curves for the polymers PP200-X, PP400-X and PPW200-X were obtained, using 20–30 mg samples which were not desiccated previously. The data are depicted as % weight loss of polymer as a function of temperature in Fig. 4. While the curve for PEG-200 (liquid) had a single stage weight loss around 260°C, the weight loss curves for the PP200-X and PP400-X polymers indicate two stage weight loss, one around 260°C and the other around 360°C; the former corresponds to the degradation of PEG [8] and the latter to that of PAAm [9]. A degradation independent of the other constituent indicates that the systems are essentially mixtures. However, the data show more unusual features. For PP200-1, the PEG-200 degradation is lowered by about 40°C. For PPW200-1, 2 and 3, and PP400-1 the degradation of PEG-200/PEG-400 occurs at 10°C below that of the pure component while that for the PAAm rises from 360 to 380°C.

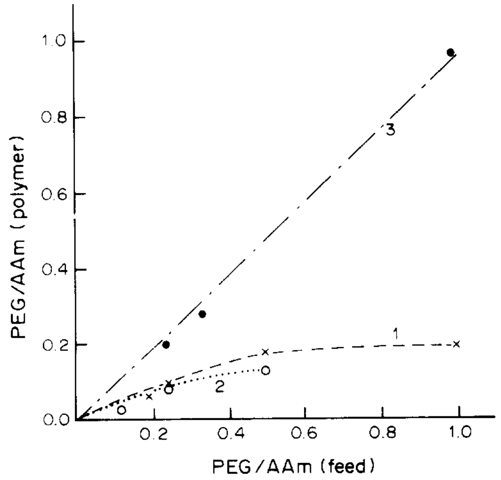

Fig. 3. Mole ratio of PEG/AAm in polymer before reprecipitation and feed: PP200-X (1), PP400-X (2) and PPW200-X (3).

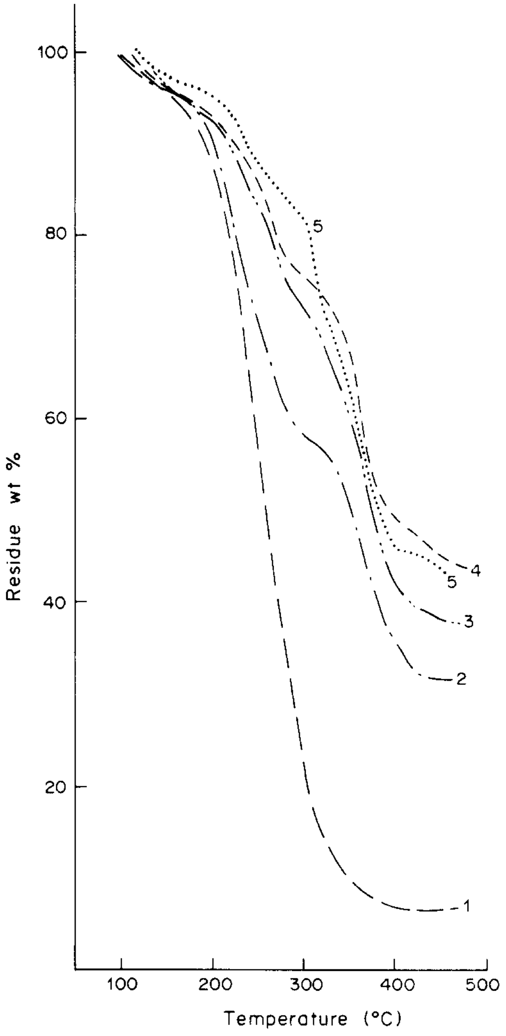

Fig. 4. Weight loss of PP200-X polymers with temperature: PEG-200 (1), PP200-2 (2), PP200-3 (3), PP200-4 (4) and PP200-1 reprecipitated (5).

Dissolution studies

Equal amounts of PP200-4 and PP400-3 were suspended in equal volumes of water and aliquots of the supernatant polymer solution after gentle shaking were collected at predesignated time intervals; synthetic boundary experiments were run in a double sector cell.

The area of the peak in the Schlieren run is a measure of the concentration of the solute [10]. The areas measured on a Nickon profile projector revealed that, at 30 min after the addition of solvent, PP400-3 had a greater solubility (area = 13.0 cm^2)

than PP200-4 (area = 10.3 cm^2). Thus it can be deduced that a longer chain length of PEG can bring about faster dissolution of PAAm [1]. It can also be noted here that PP400-3 has a higher intrinsic viscosity (185 ml g^{-1}) than PP200-4 (89.4 ml g^{-1}), and both have almost equal occlusion of ethylene glycol, (mole ratio of ethylene oxide to acrylamide, 0.20). However, the polymers obtained in the aqueous medium have markedly slower dissolution as compared to the above systems even though larger amounts of PEG are occluded in them.

Furthermore, the non-removal of the last traces of PEG, particularly in PPW200-X polymers even after 3–4 reprecipitations as identified from NMR and i.r. imply the possibility of grafting in these polymers.

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