

Poly(ethylene glycol) block copolymers by redox process: kinetics, synthesis and characterization

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Abstract: Novel block copolymers of poly(ethylene glycol) (PEG) with various vinyl monomers namely acrylonitrile (AN), acrylamide(AAm), methyl methacrylate (MMA) and methacrylic acid (MAA) were synthesized using Ce^{4+} -PEG and Mn^{3+} -PEG redox system in aqueous acidic medium. The polymerization proceeded via a macroradical generation, which was substantiated by ESR spectroscopy. This macroradical acted as a redox macroinitiator for the block copolymerization of vinyl monomers. The formation of the block copolymers was confirmed by chemical test and fractional precipitation, as well as by FT-IR, 1H & ^{13}C FT-NMR spectroscopy. The triblock nature of the block copolymers was established through the cleavage of the ether linkage of the PEG segments.

INTRODUCTION

Block copolymers are macromolecules comprising of chemically dissimilar and terminally connected segments. They provide one of the most exciting classes of materials, since the appropriate design of the block copolymer architecture with segments of various chemical composition results in interesting physico-chemical properties. In recent times, block copolymers containing both hydrophilic and hydrophobic blocks have received much attention from the biomedical point of view (ref. 1). Poly (ethylene glycol) (PEG) is one of the common hydrophilic polymers studied, which has potential for application in a variety of fields such as biological science, biomedical science, surface chemistry and electrochemistry (ref. 2).

The synthesis of block copolymers represent an additional method of production of new materials besides the synthesis of new monomers and polymers, and their physical blends. Most of the block copolymers have been prepared by ionic (usually anionic) methods. Preparation by free radical polymerization potentially represents a useful alternative synthetic approach, as it is applicable to many more monomeric species and is comparatively less expensive and easier to handle than ionic methods. In recent years, besides the various synthetic methods, redox initiating systems have been successfully used for the synthesis of block copolymers via radical mechanism (ref. 3-5). These redox systems have the advantage of performing at reasonable rates under moderate temperatures.

The essence of redox initiation is an oxidation-reduction reaction. In this process, free radicals are produced by the oxidation of the substrate, which then initiate the polymerization. Commonly employed oxidants are $Ce(IV)$, $Mn(III)$, $V(V)$, $Cr(IV)$, $Co(III)$, $Fe(III)$, etc. These oxidants form effective redox systems with various reducing agents like alcohols, aldehydes, ketones, acids, amines, amides, thiols, etc. for the aqueous polymerization of vinyl monomers. The use of a polymeric substrate as a reducing agent in a redox system results in the formation of a macro radical, which is capable of initiating vinyl polymerization.

The present paper describes about the novel synthesis of PEG block copolymers with various vinyl monomers from Ce^{4+} -PEG and Mn^{3+} -PEG redox systems as part of our ongoing investigations. This method of block copolymerisation could also be used for the preparation of emulsion at room temperature (ref. 6). The potential uses of these polymers for other application is under investigation.

EXPERIMENTAL

Kinetic measurements:

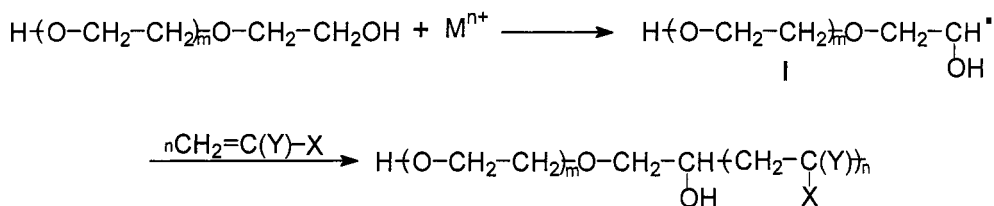
The kinetic studies were carried out as per the procedures documented in our earlier reports (ref. 7-10). The experiments were carried out in nitrogen atmosphere and in unstirred conditions. The reaction was initiated either by Ce^{4+} or Mn^{3+} and terminated by ferrous ammonium sulphate solution.

Polymerisation:

The synthesis of block copolymers were carried out in aqueous medium as per our earlier reports (ref. 11-13). All the polymerisation experiments were carried out under nitrogen atmosphere. After polymerisation the soluble polymers were precipitated from acetone. The precipitated polymers were washed several times with water to remove any unreacted PEG, monomer and initiator and then dried under vacuum at 60-70°C.

RESULTS AND DISCUSSION

The block copolymerization is proposed to proceed through the formation of an intermediate macroradical, which acts as a macroinitiator for the polymerization of the vinyl monomer, as shown in the scheme below.



where $\text{M}^{n+} = \text{Ce}^{4+}, \text{Mn}^{3+}$

$\text{X} = \text{COOH}, \text{COOCH}_3, \text{CONH}_2, \text{CN}$

$\text{Y} = \text{H}, \text{CH}_3$

Similarly the polymerization of the vinyl monomers can proceed from the other end of PEG also. The formation of the intermediate radical has been authenticated by ESR spectroscopy using POBN as the spin trap at room temperature. The short-lived free radicals were trapped by α -(4-pyridyl-1-oxide) N-tert-butyl nitron (POBN) to generate nitroxyl radicals that were sufficiently stable to be measured by ESR. The trapped radicals were determined according to the characteristic values of the hyperfine splitting constants of nitrogen and β -hydrogen. The ESR spectrum of ceric ammonium nitrate(CAN)/PEG/POBN system at room temperature is shown in Figure-1, which shows three lines of equal intensities and the coupling constant is found to be $5.5 \times 10^{-4}\text{T}$. This implies the formation of the initial free radical I, which reacts with POBN to form the spin adduct shown in Figure-1. The radical I in the absence of any vinyl monomer is subsequently oxidised to yield a long chain aldehyde.

Kinetic studies:

Kinetics of the metal ion (M^{n+})-PEG redox couple initiated polymerization for the metal ions Ce^{4+} and Mn^{3+} have been studied and reported. The polymerization in these cases proceeded without an induction period in dark and was inhibited by oxygen, indicating the free radical nature of the reaction. The rates were enhanced markedly if the system was exposed to diffused daylight. The rates under unstirred conditions were found to be greater than those under stirred conditions, which has been attributed to the greater probability of encounters between the chain radicals and the terminating agent under stirred conditions. The rate of monomer disappearance was found to be dependent on the square of monomer concentration and first power of PEG concentration, and independent of both M^{n+} and H^+ concentrations. The rate of ceric ion disappearance was dependent on M^{n+} and H^+

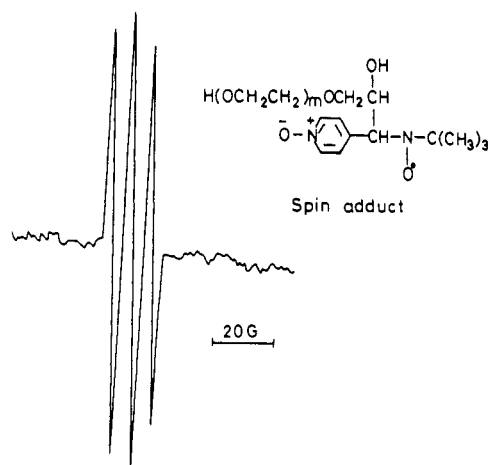


Figure-1 ESR spectrum of CAN/PEG/POBN at room temperature

concentrations, but independent of monomer concentration. Appropriate kinetic scheme and mechanism were evaluated based on the foregoing observations. The kinetic features were found to be analogous in both Ce^{4+} and Mn^{3+} systems.

Fractional precipitation studies:

Fractional precipitation experiments were carried out to confirm the exclusive formation of block copolymers. Percentage of precipitated amounts of polymers are plotted against increasing volume ratios, Y , of precipitant to solvent. Figure-2 shows the fractional precipitation curves for polyacryl amide (PAAm) and PAAm-b-PEG20000-b-PAAm. The precipitation ranges (in terms of volume fractions of acetone, Y values) are found to be 0.66 to 0.70 (for PAAm) and 0.80 to 0.84 (for PAAm-b-PEG20000-b-PAAm). Precipitation studies of a physical mixture of the homopolymers and the block copolymers (50 wt.% of each polymer) were also carried out in both cases to confirm the absence of homopolymers in the product.

Reactivity of the two ends of PEG is considered to be of the same order and hence the possibility of formation of a diradical is more, which will result in the formation of a triblock copolymer rather than a diblock copolymer. The formation of triblock copolymer is confirmed by treating the block copolymer with Hydrogen Iodide (HI) solution. As the block copolymer contains ether linkages in the PEG segment, we anticipate its cleavage when treated with HI. If the polymer is a diblock copolymer, on cleavage there should not be any appreciable change in the molecular weight excepting for the molecular weight of PEG which undergoes cleavage. On the other hand if the polymer is of triblock nature, cleavage of the PEG unit should result in two polymeric units of approximately equal molecular weight which is more or less half the value of the original block copolymer molecular weight. GPC results show that the molecular weight of the block copolymer reduced to about half that of the original polymer molecular weight. This positively indicates that the original block copolymer is a symmetric triblock copolymer.

Spectroscopic studies:

Fourier transform infrared spectroscopy is used to study the formation of block copolymers. The FT-IR spectra showed characteristic bands for the various block copolymers synthesized. A representative FT-IR spectrum for the system PEG20000-b-PAN is shown in Figure-3. The FT-IR spectrum showed characteristic absorption bands for -C-O-C- stretching vibration at 1115 cm^{-1} and -CN stretching vibration at 2240 cm^{-1} . Similar observations were noted in the other block copolymers also. In the case of PEG-b-PMMA the ester carbonyl stretching was observed at 1734 cm^{-1} , and similarly for PEG-b-PAAm the amide carbonyl appeared at 1666 cm^{-1} . All the above results confirm the formation of the block copolymers.

FT-NMR (^1H & ^{13}C) spectroscopy has also been employed to prove the formation of the block copolymers. A typical NMR spectrum of the system PEG-b-PAN is shown in Figure-4. The ^1H -NMR spectrum (Fig. 4a) exhibits α -hydrogen peaks of the ether linkages and nitrile group at 3.38 and 2.15 ppm respectively indicating the presence of both PEG and PAN segments in the block copolymers. In the ^{13}C -NMR spectrum, the nitrile carbon resonance of the block copolymer appears at 120 ppm, the methylene carbons

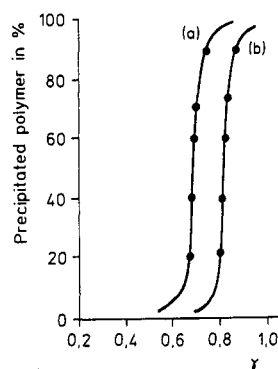


Fig. 2 Fractional precipitations of PAAm-b-PEG20000-b-PAAm. Precipitant: acetone: Solvent: water

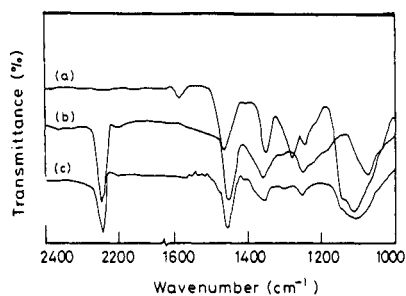


Fig.-3 FT-IR spectra of (a) PAN, (b) PEG 20,000 and (c) PEG 20,000-b-PAN

at 32.6 ppm and the methine carbon at 27 ppm. The ^1H and ^{13}C -NMR spectra of the other block copolymers were also consistent with the structure assigned.

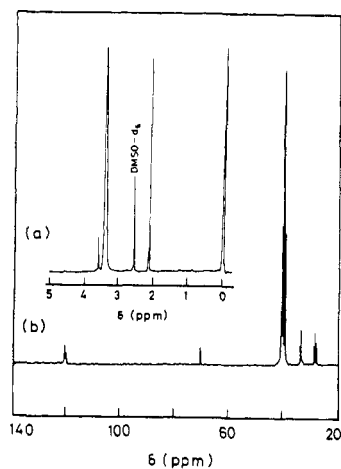


Fig. 4 ^1H (a) and ^{13}C (b) NMR spectra of PEG 20,000-b-PAN

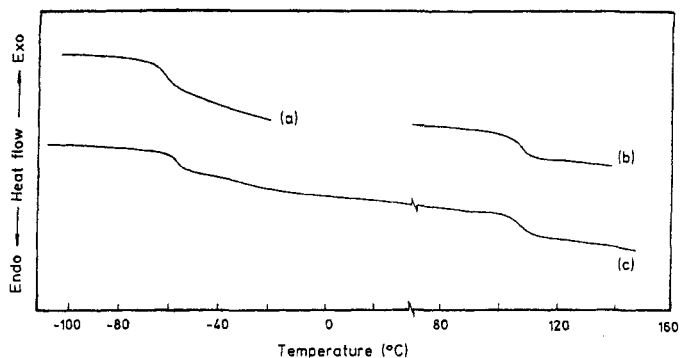


Fig. 5 DSC thermograms of (a) PEG9000, (b) PMMA and (c) PMMA-b-PEG9000-b-PMMA

DSC studies

The DSC thermograms of PEG9000, PMMA and PMMA-b-PEG9000-b-PMMA are shown in Figure-5. PEG exhibits a glass transition temperature at -64°C , while that of PMMA is observed at 110°C . In the block copolymer the Tg of PEG is observed at -48°C in addition to the Tg of PMMA at 109°C . DSC patterns of the other block copolymeric systems were also similar to the above observation.

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