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S. K. Chatterjee[a]; J. B. Yadav[a]; K. R. Sethi[a]; A. M. Khan[a]
[a] Department of Chemistry, Delhi University, Delhi, India

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STUDY OF INTERMACROMOLECULAR COMPLEX FORMATION BETWEEN ACRYLAMIDE—VINYL ALCOHOL GRAFT COPOLYMER AND POLY(METHACRYLIC ACID)

S. K. CHATTERJEE,* J. B. YADAV, K. R. SETHI, and A. M. KHAN

Department of Chemistry
Delhi University
Delhi 110007, India

ABSTRACT

Acrylamide-vinyl alcohol (AAm/VA) graft copolymer was prepared and characterized. The interaction of the graft copolymer with poly(methacrylic acid) (PMAA) in water was studied by several experimental techniques, such as viscometry, potentiometry, conductometry, IR spectra, and transmittance measurements. PMAA was found to interact with the graft copolymer in two distinct steps. The relative complexation ability of PAAm and PVA with respect to PMAA does not change when these polymers are present as parts of a graft copolymer chain.

INTRODUCTION

Intermacromolecular complexes have acquired a unique position in the field of polymer science in view of their potential applications in industry and medical biology [1, 2]. The extensive studies of these complexes are mostly confined to homopolymer-homopolymer interactions [3-9]. These interactions occur through secondary binding forces, such as H-bonding, van der Waals and electrostatic forces, hydrophobic interactions, etc. [2]. Apart from this, other factors, such as the length of the reacting chains, their flexibility, conformation, concentration, temperature, solvent, pH, degree of ionization, etc., may also influence polymer-polymer interactions considerably [2].

Some reference has been made in the literature to intermacromolecular complex formation between alternating [10, 11] and random copolymers [12, 13] with nonionic polymers, but there seems to be no mention of intermacromolecular complexes involving a graft copolymer. For this reason an acrylamide-vinyl alcohol (AAm/VA) graft copolymer was prepared [14] and characterized, and its interaction with poly(methacrylic acid) (PMAA) was studied. This system is interesting because both the component homopolymers (i.e., PAAm and PVA) are known to interact with PMAA to form interpolymer complexes [1, 2]. Hence, one would expect that cooperativity may play a significant role on the interaction between the graft copolymer and a homopolymer. The ultimate aim of this study is to see the influence of grafting on the stoichiometry of the complex and the mode of interaction between the component chains of the graft copolymer and PMAA.

EXPERIMENTAL

Poly(Methacrylic Acid) (PMAA)

Methacrylic acid (from BDH) was distilled at 12 torr (bp 63°C) and polymerized with $K_2S_2O_8$ as initiator in an aqueous medium, with a monomer concentration of about 0.2 mol/L for 5 h under nitrogen at 50°C. The reaction mixture was evaporated, dissolved in methanol, and reprecipitated twice with ethyl acetate. The molecular weight ($\bar{M}_w$) of the polymer, calculated from viscosity measurements in methanol at 25°C by the equation [3],

$$[\eta] = 24.2 \times 10^{-4} \bar{M}_w{}^{0.51},$$

was found to be 42 000.

Acrylamide-Vinyl Alcohol Graft Copolymer (AAm/VA)

This was prepared by grafting acrylamide onto poly(vinyl alcohol) in an aqueous medium under nitrogen at 25°C with ceric ammonium nitrate as initiator [14]. The gross copolymer was found to contain 35 mol% of acrylamide units, as determined by nitrogen estimation. The percentage of grafting was around 21%. The molecular weight ($\bar{M}_w$) of poly(vinyl alcohol), used as the main chain of the graft copolymer, calculated by the Mark-Houwink equation [15], was 14 000.

Solvent

Double-distilled water was used for all experimental measurements.

Conductometric and Potentiometric Titration

The conductometric titration was carried out with a Leeds and Northrop (Model 4959) electrolytic conductance bridge. The limit of error in the conductance measurement was ±0.15% of the reading at the high end of the mho scale, increasing to 1% of the reading at the low end. The pH was measured with an ECIL digital pH meter with a combination electrode. The resolution of the instrument was ±0.01 pH unit. Titrations were performed in a constant-temperature bath at 30°C. The concentrations of the copolymer and homopolymer solutions were in the range 1-5 nmol/L.

Infrared Spectra

The infrared (IR) absorption spectra of the interpolymer complexes were recorded with a Perkin-Elmer grating infrared spectrophotometer (Model 621). The resolution of the instrument was 5-10 cm^{-1}.

Viscosity

The viscosity measurements for various unit mole ratios at 30 ± 0.05°C were performed with an Ubbelohde viscometer for which the kinetic energy correction was negligible. Lower concentrations (i.e., 0.5 nmol/L) of copolymer and homopolymer solutions were used to avoid precipitation during viscosity measurements.

Transmittance Measurements

The percentage transmittance in mixed solutions of the component polymers was measured 5 min after mixing with a Perkin-Elmer spectrophotometer (Model 554). The sensitivity of the instrument was ±0.01% in terms of percentage transmittance.

RESULTS AND DISCUSSION

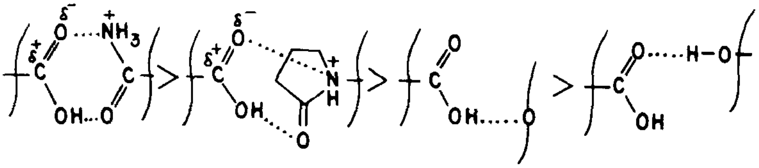
Tsuchida and coworkers [5] studied selective complexation of several nonionic homopolymers, such as poly(acrylamide) (PAAm), poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO), and poly(vinyl alcohol) (PVA) with poly(methacrylic acid) (PMAA). On the basis of Scheme 1, they suggested that the relative complexation ability of the nonionic homopolymers with respect to PMAA decreases in the following order: PAAm > PVP > PEO > PVA.

It has been argued that PAAm and PVP interact with PMAA more strongly than PEO and PVA because complex formation in the former is not only through H-bonding but also through ion-dipole interaction between partially protonated amide groups of PAAm and dipoles of >C=O of PMAA. Of course, PVP can also interact through hydrophobic interactions. On the other hand, PEO and PVA interact with PMAA primarily through H-bonding as indicated in Scheme 1.

To extend these studies, we prepared and characterized an acrylamide/vinyl alcohol (AAm/VA) graft copolymer [14].

The variation of pH, conductance, reduced viscosity, percentage transmittance, and weight of precipitate formed on adding an increasing concentration of PMAA to AAm/VA graft copolymer in an aqueous medium are depicted in Figs. 1 and 2. The pH, conductance, reduced viscosity, and transmittance curves showed two distinct breaks at 0.35:1.0 and 1.0:1.0 unit mol ratio (umr). However, the curve of weight of precipitate formed showed only one distinct break at 1.0:1.0 umr. The coincidence of these two distinct stages of interaction observed through several independent measurements strongly suggests stepwise interpolymer complex formation.

The pH curve (Fig. 1, Curve b) showed a gradual decrease in the pH throughout the addition of PMAA to the graft copolymer solution. It may be mentioned that Ikawa et al. [16] had observed an increase in pH during complex formation, which was attributed to entanglement of protons in the complex. However, their observations were mostly confined to homopoly-



SCHEME 1.

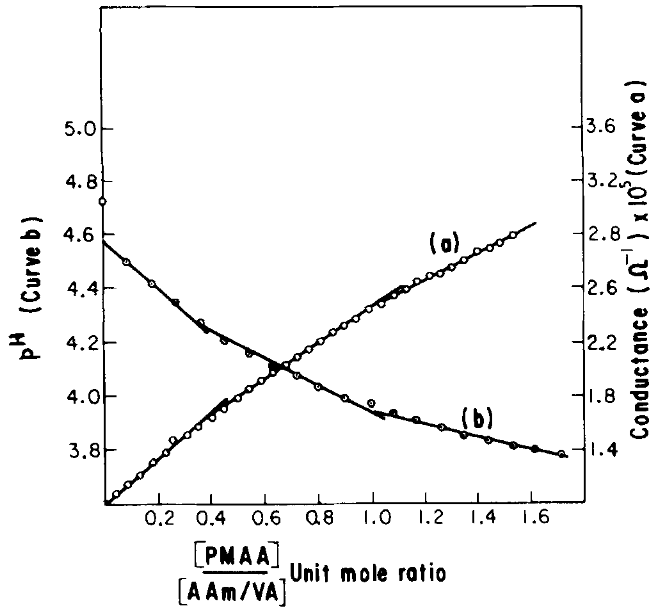


FIG. 1. Variation of conductance and pH with the unit mole ratio, PMMA:AAm/VA: (a) conductance, (b) pH.

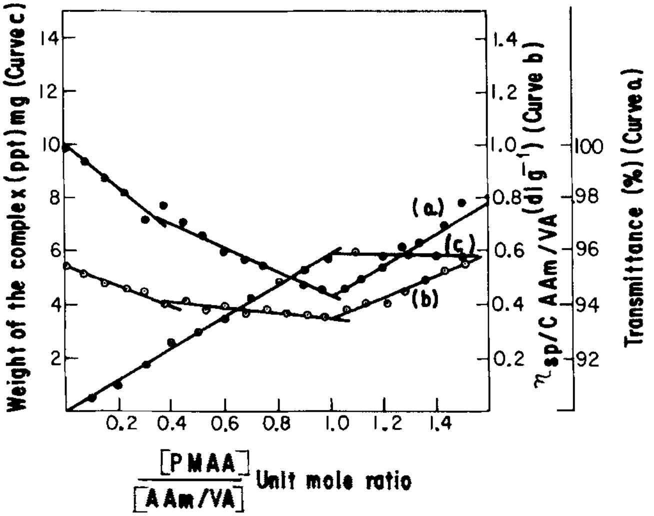


FIG. 2. Variation of transmittance, specific viscosity, and weight of the complex precipitate with the unit mole ratio, PMMA:AAm/VA: (a) transmittance, (b) specific viscosity, (c) weight of complex precipitate.

mer systems. In the present case, perhaps the protons are not bound as rigidly in the complex, and possibly the complex may be in equilibrium with its dissociated form. The addition of increasing concentration of PMAA will result in the formation of higher concentrations of complex, and consequently its greater dissociation with the simultaneous release of more protons. In fact, this is in agreement with the continuous increase in conductance with increasing concentration of PMAA (Fig. 1, Curve a).

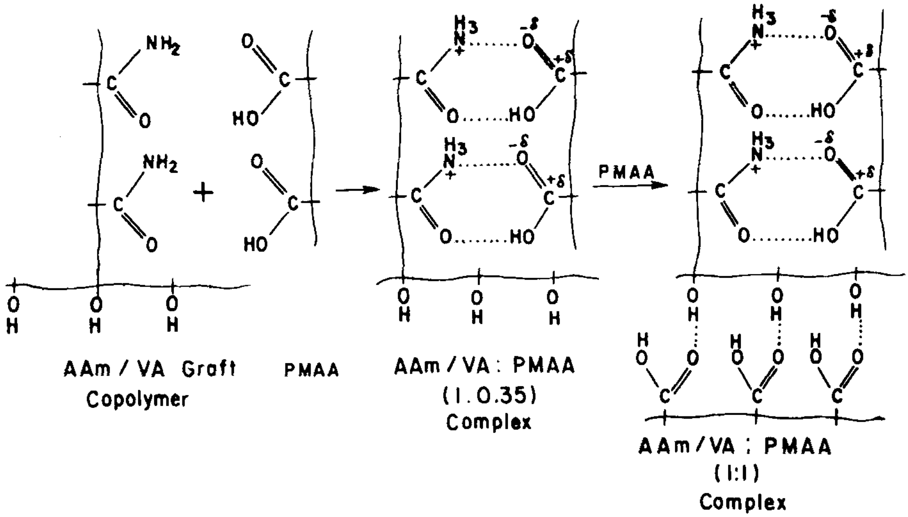
Figure 2 (Curve b) shows a continuous fall in reduced viscosity up to 0.35 umr and a lower rate of decrease up to 1.0 umr. After this, a sharp increase was observed. The nonionic graft copolymer (AAm/VA) in an aqueous medium is expected to have a reasonably extended conformation because of polymer-solvent interaction. On adding PMAA, the PAAm branches of the graft copolymer interact with PMAA, and graft copolymer probably changes to a more compact conformation, accounting for the fall in reduced viscosity. The subsequent interaction of PMAA with the main chains (i.e., PVA) of the graft copolymer apparently makes the coiled structure even a little more compact, as reflected by a further fall in reduced viscosity. The increase in reduced viscosity beyond 1.0 umr appears to be due to excess uncomplexed PMAA.

Figure 2 (Curve a) shows a drop for both stages of interaction, and when complex formation is complete beyond 1.0 umr, the transmittance increases, possibly due to dilution of the complex. The plot of weight of complex precipitated (Fig. 2, Curve c) shows no break at 0.35 umr.

Due to the stronger complexation ability of the acrylamide units (AAm) of the graft copolymer chains, these units interact preferentially with the MAA units of PMAA. Since the graft copolymer contains 0.35 um AAm units, the first break (or inflection) at 0.35 umr in the titration curves could be assigned to the interpolymer complex between AAm and MAA units with a stoichiometry of 1.0:1.0 umr. The subsequent break (or inflection) at 1.0 umr then indicates that both the comonomer units are involved in the complex formation with identical stoichiometry (i.e., AAm:MAA and VA:MAA = 1.0:1.0).

A plausible scheme of the postulated two-step complexation may be suggested on the basis of these observations (Scheme 2).

The IR spectra of the two interpolymer complexes were compared with those of PMAA and AAm/VA graft copolymer. The $\nu_{C=O}$ frequency, observed at 1730 cm^{-1} for pure PMAA, shifted to 1630 cm^{-1} for the 0.35:1.0 interpolymer complex. AAm/VA in the pure state had a sharp band at 3440 cm^{-1}, which indicated the presence of intramolecular H-bonding. In the 1.0:1.0 complex this band, observed at 3480 cm^{-1}, was quite broad, showing the probable involvement of vinyl alcohol (VA) units of the graft



SCHEME 2.

copolymer in the second stage of interaction. Thus the stepwise interaction of PMAA with the AAm/VA graft copolymer agrees with the shifts of the IR group frequencies. This stepwise interaction is expected in view of the stronger complexation ability of AAm units than of VA units for the MAA units of the graft copolymer [5].

In order to see the influence of grafting on interpolymer complex formation, we examined a mixture of PAAm and PVA in the same proportion as in the graft copolymer. The pH and specific viscosity curves of the mixture corresponded to those of the graft copolymer. However, the conductance curve of the mixture showed a fall during the interaction of PMAA with PAAm chains, in contrast to the behavior of the graft copolymer. This could possibly be interpreted on the basis of a more compact structure of the graft copolymer molecules as a result of interaction with PMAA. However, the IR spectra of the complexes obtained from the graft copolymer and the homopolymer mixture did not indicate any striking difference.

In conclusion, it can be said that neighboring comonomer units could possibly influence copolymer-homopolymer interactions. The relative complexation ability of the two nonionic polymers PAAm and PVA with respect to PMAA does not charge, even when these component polymers are present as parts of a graft copolymer chain.

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