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Selective Interpolymer Complexation between Acrylic Copolymers and Nonionic Polymers

S. K. Chatterjee[a]; A. Malhotra[a]

[a] Department of Chemistry, University of Delhi, Delhi, India

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S. K. CHATTERJEE and A. MALHOTRA

Department of Chemistry
University of Delhi
Delhi 110007, India

ABSTRACT

Selective interpolymer complexation has been studied between methacrylic acid-methacrylamide copolymer and some complementary polymers such as poly(methacrylamide), poly(vinyl pyrrolidone), and poly(ethylene oxide). The relative order of complexation ability of the various nonionic polymers has been interpreted on the basis of the nature of interactions between different units of polymers. Configurational environment and neighboring group influences seem to affect interpolymer complex formation.

INTRODUCTION

Selective complexation between macromolecules is an important phenomenon in biological systems [1, 2]. Although it is not clearly understood how the macromolecular chain effectively selects a complementary one in order to perform specific functions, it was thought by some early workers that selective complexation between synthetic polymers of known characteristics may provide an excellent model system to simulate biological processes [3, 4]. Tsuchida and co-workers [5] studied some selective interpolymer complexation re-

actions involving polycarboxylic acids and some nonionic polymers. However, no reference seems to be available in the literature regarding the use of acrylic copolymers in selective interpolymer complexation, although complexation involving alternating [6] and random [7] copolymers with nonionic polymers has been reported in the literature. Acrylic copolymers containing methacrylic acid (MA) and methacrylamide (MAm) units in the chain are interesting systems in view of the fact that these units form a stable interpolymer complex when present as homopolymers [8]. Therefore, one can expect inter- as well as intrachain interactions when these copolymers react with nonionic polymers. Moreover, one can expect the influence of cooperative and neighboring group interactions to be more predominant in the case of copolymers compared to homopolymers. Keeping this objective in mind, we have studied the selective interpolymer complexation involving (MA/MAm) copolymer and such nonionic homopolymers as poly(methacrylamide) (PMAm), poly(vinyl pyrrolidone) (PVP), and poly(ethylene oxide) (PEO).

EXPERIMENTAL

Poly(ethylene Oxide) (PEO)

PEO was supplied by Iwai Kagaru Co., Japan, and its weight-average molecular weight ($\overline{M}_w$) was found to be 1.9×10^4 as calculated from a viscosity equation [9].

Poly(vinyl Pyrrolidone) (PVP)

PVP was supplied by Fluka, U.S.A. The $\overline{M}_w$ of the polymer was calculated from a viscosity equation [10].

Poly(methacrylamide) (PMAm)

PMAm was prepared by the free radical polymerization mechanism, using $K_2S_2O_8$ as the initiator. The polymerization was carried out in water at 70°C for 45 min. The polymer was separated as white solid mass at the end of the polymerization and was purified by washing several times with nonsolvent acetone.

Methacrylic Acid/Methacrylamide (MA/MAm) Copolymer

Copolymer (MA/MAm) was prepared by free radical polymerization using $K_2S_2O_8$ as the initiator [11]. MA and MAm were taken in the ratio 9:1 (w/w) in an aqueous medium (100 mL) with 0.1% $K_2S_2O_8$, and heated in a nitrogen atmosphere at 70°C for 50 min. As soon as the product precipitated, it was separated and dissolved in acetone and reprecipitated with ether. The process was repeated thrice to remove unreacted monomers. The composition of the copolymer was determined by electrometric titration techniques [12] and was found to have monomeric units in equal amounts (i.e., ~50% MA and ~50% MAm).

Solvent

Double distilled water was used as solvent for all experimental measurements.

Viscosity

The viscosity of the mixed solution of copolymer (MA-MAm) (1×10^{-3} to 5×10^{-3} unit mol/L) with PVP, PMAm, and PEO (1×10^{-3} to 5×10^{-3} unit mol/L) at various unit mole ratios was determined at 30 ± 0.05°C by an Ubbelohde viscometer for which the kinetic energy correction was negligible.

Potentiometric Titration

pH titrations were carried out with a Radiometer pH meter (model PHM 26 C) using glass (G 202 B) and calomel (K 401) electrodes. The pH of the mixed solutions was measured at various unit mole ratios. The reproducibility of the values was checked and found to be within ±2%.

Conductometric Titrations

Conductometric titrations were carried out with a Leeds and Northrup (4959) conductance bridge. The concentration of the copolymer and the homopolymer solutions used in both the conductance and pH titrations were of the same order as in the viscosity experiment.

RESULTS AND DISCUSSION

Studies on selective interpolymer complex formation between proton-donating polymers, such as poly(methacrylic acid) (PMA), and proton-accepting polymers, such as poly(methacrylamide) (PMAm), poly(vinylpyrrolidone) (PVP), and poly(ethylene oxide) (PEO), revealed that the complexation ability of these nonionic polymers follows the order [5] PMAm > PVP > PEO.

The stronger complexation ability of PMAm is explained by the fact that PMAm forms complexes with PMA not only through H-bonding but also through ion-dipole interactions between partially protonated amide groups of PMAm and the $>C=O$ dipole of the carboxyl groups of PMA [2]. In the case of complexation with PVP, hydrophobic interactions are also assumed to play an important role, whereas PEO enters into complexation with PMA only through H-bonding [2]. Some preliminary investigations from this laboratory indicated that PMA chains can interact with two complementary polymers (e.g., PVP and PEO) consecutively to form a ternary complex, and replacement of one component by another component in the complex is possible by adding the polymer of stronger complexing ability in excess [13].

In order to see the behavior of the various nonionic polymers (e.g., PMAm, PVP, and PEO) during complexation with MA units present in a copolymer chain with methacrylamide (MAm) units, the complementary polymers were mixed in definite stoichiometric unit mole (um) ratios, and (MA/MAm) copolymer solution was added to the mixture. Figure 1 shows the variation of reduced viscosity (η_{sp}/c), conductance, and pH of the mixed nonionic polymer solutions (i.e., 0.2 PMAm + 0.4 PVP + 0.5 PEO) (um) on the addition of increasing concentrations (um) of copolymer. The copolymer (MA/MAm) has been characterized by electrometric titration techniques [12] and found to have around 50% each of MA and MAm units. The identical unit molecular weight of both the units (i.e., MA and MAm) is an additional advantage associated with this copolymer. An abrupt fall in the reduced viscosity (cf. Curve A of Fig. 1) has been observed up to a 0.4 unit mole ratio (umr), $\left(\text{i.e., } \dfrac{[Cop]}{[PMAm] + [PVP] + [PEO]} \right)$, and the reduced viscosity (i.e., η_{sp}/c) subsequently tends to increase slightly up to 0.8 (umr), and then again decrease to 2.2 (umr), with a distinct break in between at 1.2 (umr). Considering the relative complexation ability of nonionic polymers, it can obviously be inferred that up to 0.4 (umr), PMAm chains in the mixture are interacting with the copolymer to form a 1:1 (umr) complex. The concentration of the copolymer consumed at the first stage is twice as large (i.e., 0.4 um) because half of its units are noninteracting with respect to PMAm homopolymer. It is also predicted that the MAm units of the copolymer simultaneously form a complex with 0.2 (um) of PVP. Because water is a good solvent for all these nonionic polymers, a reasonably extended confor-
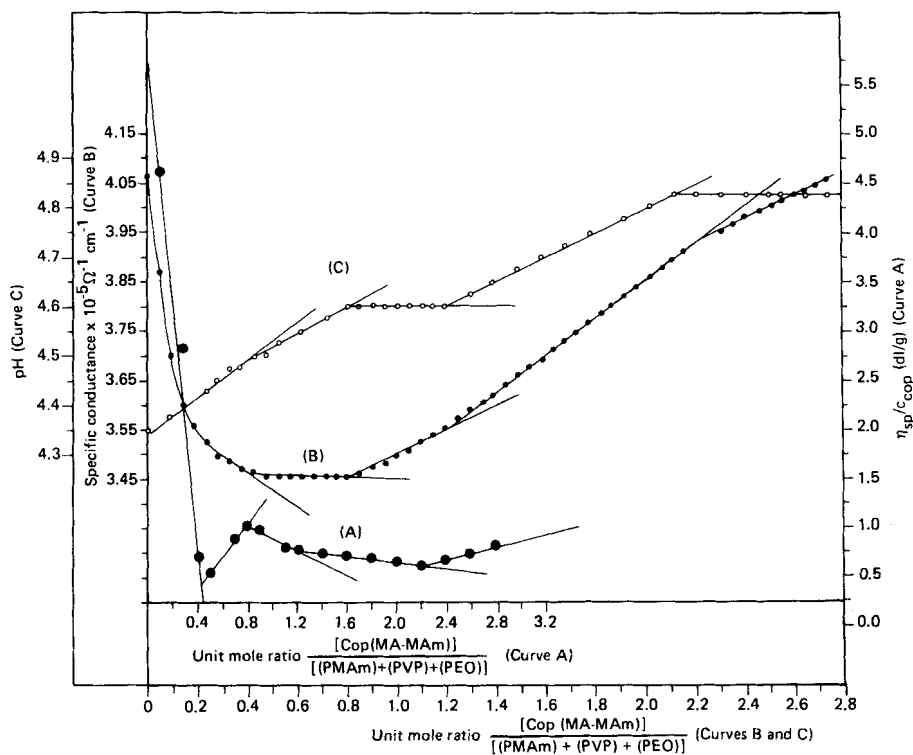
FIG. 1. Variation of reduced viscosity, conductance, and pH with unit mole ratio, $\dfrac{[Cop]}{[PMA] + [PVP] + [PEO]}$. (A) Reduced viscosity, (b) conductance, (C) pH.

mation can be assumed for all these polymers in aqueous medium. On the addition of the copolymer solution, the nonionic polymer chains possibly become more compact as a result of interaction with MA as well as MAm units of the copolymer. This is probably reflected by the very sharp fall in the reduced viscosity (cf. Curve A of Fig. 1). Further addition of copolymer (i.e., up to 0.8 um) increases the reduced viscosity, which obviously indicates that the remaining 0.2 um of PVP present in the mixture is interacting with MA units of the copolymer chain to form a 1:1 complex. Because of the presence of noninteracting units in the copolymer chain, the complex molecule can be expected to be a little more rigid, and this may be attributed to the increase in viscosity at this stage. Surprisingly, the next step (i.e., at 1.2 um) in the viscosity curve is not due to complexation with PEO chains. The weak interaction between PVP and MAm units of the copolymer chain (i.e., at the first stage) probably breaks up on adding

more of the copolymer, and is ultimately substituted for by the stronger
1:1 PVP-PMA(Cop) complex. The final break in the viscosity curve
(cf. Curve A of Fig. 1) occurs at 2.2 (um), which can be attributed to
1:1 complex formation between 0.5 (um) PEO and 1.0 (um) copolymer.
It should be mentioned once again that 1.0 (um) copolymer gives an ef-
fective concentration of 0.5 (um) MA units. The increase in reduced
viscosity beyond 2.2 (um) can obviously be attributed to excess co-
polymer.

An excellent correlation between different stages of interaction be-
tween the (MA/MAm) copolymer and the nonionic polymer mixture can
also be obtained from conductance and pH measurements (cf. Curves
B and C of Fig. 1). The abrupt fall in conductance or the correspond-
ing increase in pH can be attributed to the entanglement of partially
protonated amide groups of PMAm [2]. The constant region and the
subsequent increase in the conductance curve (cf. Curve B of Fig. 1)
can be interpreted on the basis of replacement of a less conducting
species by a more conducting species, i.e., the complexed molecules
are expected to be smaller (i.e., more compact) and may also carry
some charge due to the polyelectrolyte character of the copolymer.
However, entanglement of protons during complexation may be re-
sponsible for the continuous increase in pH (cf. Curve C of Fig. 1).

It is known that the configurational environment during complex
formation influences the stoichiometry of the interpolymer complex
[14, 15]. Moreover, we thought that a ternary or a quaternary com-
plex could be formed by adding different stoichiometric amounts of
the various nonionic polymers to a known concentration of the copoly-
mer. Keeping these objectives in mind, we studied the variation of
reduced viscosity, conductance, and pH of a (1.0 um) copolymer solu-
tion by adding 0.2 (um) PMAm, 0.3 (um) PEO, and excess PVP solu-
tion, respectively (cf. Fig. 2). The viscosity curve (cf. Curve A of
Fig. 2) showed a steep fall up to 0.5 (um), i.e., $\dfrac{[PMAm] + [PEO]}{[Cop]}$,
obviously indicating complexation of PMAm and PEO with the MA
units of the copolymer chains. Thereafter, on addition of excess PVP
solution, the reduced viscosity continued to fall, though at a slower
rate, up to 1.3 (um), indicating interaction of PVP with the MAm units
of the copolymer chain along with the replacement of PEO in the com-
plex by PVP. However, both conductance and pH curves (cf. Curves
B and C of Fig. 2) indicated stepwise interactions of copolymer with
PMAm, PEO, and PVP, and also that the substitution reactions occurred
in distinct steps. Of course, some of the steps do merge in the viscos-
ity curve. The simultaneous increase in conductance and pH during
complexation can be attributed to the reasons mentioned in the earlier
part of the discussion.

On the basis of these results, the complexation between different
units may be described as follows:
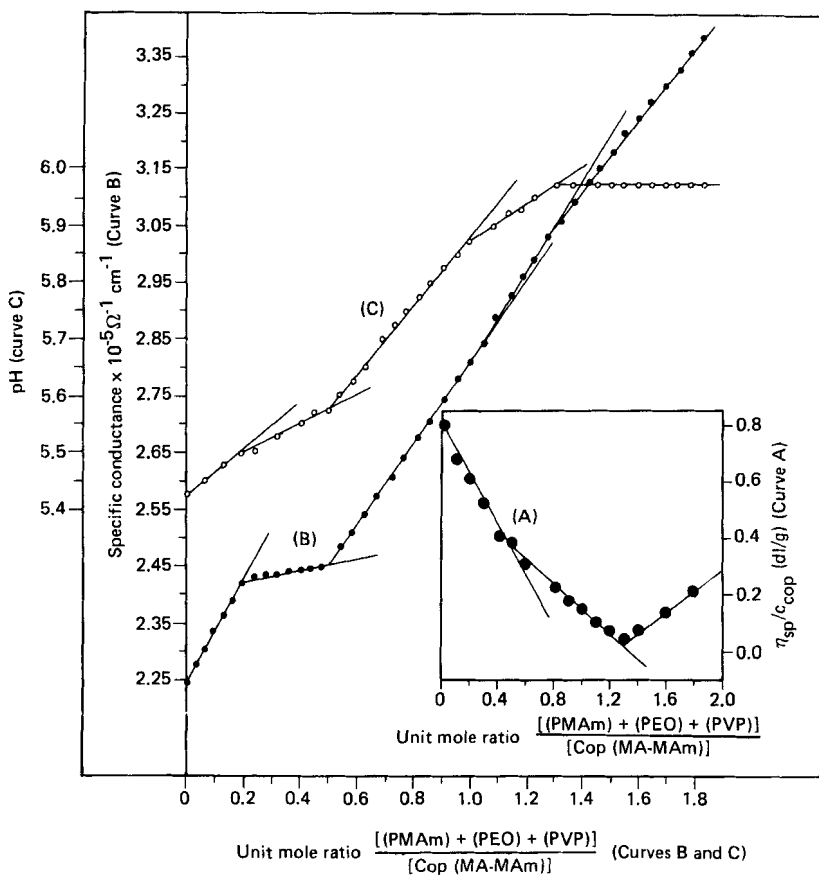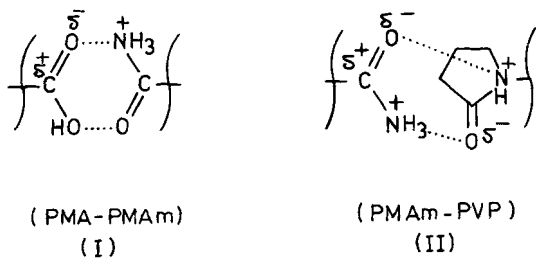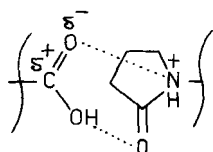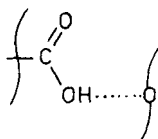
(PMA-PMAm)
(I)

(PMAm - PVP)
(II)

FIG. 2. Variation of reduced viscosity, conductance, and pH with unit mole ratio, $\dfrac{[\text{PMAm}] + [\text{PEO}] + [\text{PVP}]}{[\text{Cop}]}$. (A) Reduced viscosity, (B) conductance, (C) pH.

(PMA-PVP)   (PMA-PEO)
(III)   (IV)

In conclusion it can be said that from selective interpolymer complexation studies, one can obtain the relative order of complexation ability of various nonionic polymers with respect to (MA/MAm) copolymer. Moreover, the same copolymer molecule can interact simultaneously with two or three different nonionic polymers to form a ternary or a quaternary interpolymer complex. Although PVP does not interact with PMAm homopolymer, MAm units in a copolymer chain distinctly enter into complex formation with PVP units, probably due to a neighboring group influence.

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