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Influence of Grafted Chain Length of a Phenolic Copolymer on Its Complex Formation with Poly(vinyl Pyrrolidone) and Poly(ethylene Oxide)

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ABSTRACT

A phenolic copolymer has been grafted with oligomers of different chain lengths. Polymer-polymer complexation has been studied between graft copolymers and nonionic polymers, such as poly(vinyl pyrrolidone) and poly(ethylene oxide), in an acetone-methanol mixture by several methods, e.g., viscosity, conductance, and apparent pH measurements. A distinct stepwise complexation between PVP and graft copolymers has been observed. The length of the side chain also seemed to influence interpolymer complex formation. Some of these observations have been interpreted with reference to the actual structure of the graft copolymers.

INTRODUCTION

Study of polymer-polymer interactions is important both from the scientific and practical points of view [1]. Interpolymer complexes are formed as a result of such interactions, and they possess unique properties which are essentially different from those of the component polymers. It is well known that interpolymer complex formation takes

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place through hydrogen bonding or ion-dipole interactions, but in addition secondary binding forces, such as hydrophobic interactions, or the degree of dissociation of carboxylic groups in a polyacid chain, are also known to influence the complex formation between two polymers [2]. Although extensive work has been reported in the literature on the numerous aspects of the study of interpolymer complexes, there seems to be very little reference regarding the use of phenolic copolymers as one of the components in the study of complex formation between polymers. The unique properties of phenolic copolymers and oligomers have been attributed to the presence of intramolecular hydrogen bonding [3-7], and it is likely that such bonding may greatly influence the ability of phenolic copolymers to form complexes with nonionic polymers like polyvinylpyrrolidone (PVP) and poly(ethylene oxide) (PEO). Some preliminary work from this laboratory on complexation of linear phenolic copolymers with PVP and PEO indicated a distinct stepwise complex formation with nonionic polymers [8, 9]. Therefore it was considered of interest to see the probable mode of complex formation between a grafted phenolic copolymer chain with PVP and PEO. Not much information seems to be available in the literature regarding complex formation involving graft copolymers. In the present paper the authors discuss how the length of the grafted chain in a phenolic copolymer can influence complex formation with nonionic polymers (e.g., PVP and PEO).

EXPERIMENTAL

Polyvinylpyrrolidone (PVP). PVP was supplied by BDH Chemicals Ltd., Poole, England. Its weight-average molecular weight ($\overline{M}_w$) was determined by the equation $[\eta] = 6.76 \times 10^{-2} M^{0.55}$ [10] (in aqueous solution at 25°C), and was found to be 3.75×10^4.

Polyethylene Oxide (PEO) was obtained from Iwai Kagaru Co., Japan, and was characterized by a viscosity equation [11]. Its weight-average molecular weight was 1.9×10^4.

Grafting of poly-p-Bromophenol-Formaldehyde Copolymer (PPF). PPF was prepared and characterized by known methods [12], and its average DP was ~12. It was dehalogenated and then grafted with specific oligomers of known structure and molecular weight. Phenolic monomers, dimers, and trimers were grafted on PPF chains under suitable experimental conditions [12, 13].

Solvent. An acetone (A)-methanol (M) mixture in the volume ratio of 84% A to 16% M was used to dissolve all the above polymers. All the measurements were made in this solvent mixture.

Viscosity. The viscosities of mixed solutions of grafted copolymers (1.0×10^{-2} unit mol/L) with PVP (5.0×10^{-4} unit mol/L) or with PEO (1.0×10^{-3} unit mol/L) at different mole ratios were measured with an Ubbelohde viscometer (kinetic energy correction negligible) at 30 ± 0.05°C.

pH Titration. The apparent pH measurements at various stages of mixed solutions of grafted copolymer (1.0×10^{-2} unit mol/L) and PVP (1.0×10^{-3} unit mol/L, or PEO (2.5×10^{-2} unit mol/L) were carried out using a Radiometer pH meter (model PHM 26 C) with a glass electrode (G 202 B) and a calomel (K 401) electrode.

Conductometric Titration. The conductometric titrations were performed with a Leeds and Northrup Conductance Bridge (4959).

RESULTS AND DISCUSSION

It is known that in polymer-polymer complexation, if one of the constituents is a low molecular weight polymer or oligomer, then the complex formation will be influenced by temperature, concentration, medium, and the chain length of the oligomer or low molecular weight polymer [14]. Keeping this fact in mind, we studied the interpolymer complex formation of PVP with phenolic copolymers having different grafted chain lengths. Figures 1 to 3 show variation of reduced viscosity, apparent pH, and conductance during complex formation of PVP with monomer grafted (MPPF), dimer grafted (DPPF), and trimer grafted (TPPF) phenolic copolymers, respectively. All the measurements were made in an acetone-methanol mixture (84% A and 16% M by volume). The component polymers were found to be completely soluble in this solvent mixture. The grafted phenolic copolymers (e.g., MPPF, DPPF, and TPPF) were found to interact with PVP in several distinct stages as evidenced by the sharp changes in viscosity, conductance, and apparent pH of the mixed solutions at specific unit molar ratios (e.g., [MPPF]/[PVP] or [DPPF]/[PVP] or [TPPF]/[PVP]). The interpolymer complexes of various unit molar ratios (i.e., [graft copolymer]/[PVP]) obtained from the distinct steps of several measurements are summarized in Table 1.

When any one of the grafted copolymers (e.g., MPPF or DPPF or TPPF) was added to PVP dissolved in the mixed solvent, an abrupt fall in reduced viscosity was observed until the unit molar ratio, i.e., [graft copolymer]/[PVP], was 0.25 or 0.33. However, a similar fall in reduced viscosity was also observed at a 0.5:1 (unit molar ratio) when linear PPF formed a complex with PVP [8]. The fall in viscosity at a lower unit molar ratio of the graft copolymer can be attributed to branched chains which, apart from increased cooperation, are also likely to make the PVP units more accessible to phenolic units for interaction. Consequently, the complex molecules are expected to be more compact (i.e., highly coiled). PVP in mixed solvent is expected to be in a reasonably extended conformation due to preferential solvation by methanol (good solvent). It is probable that, initially, certain interacting sites of PVP bind with the grafted phenolic copolymer by chance [14]. This binding may be due to donation of hyperacid proton of grafted copolymer to the tertiary N atom of

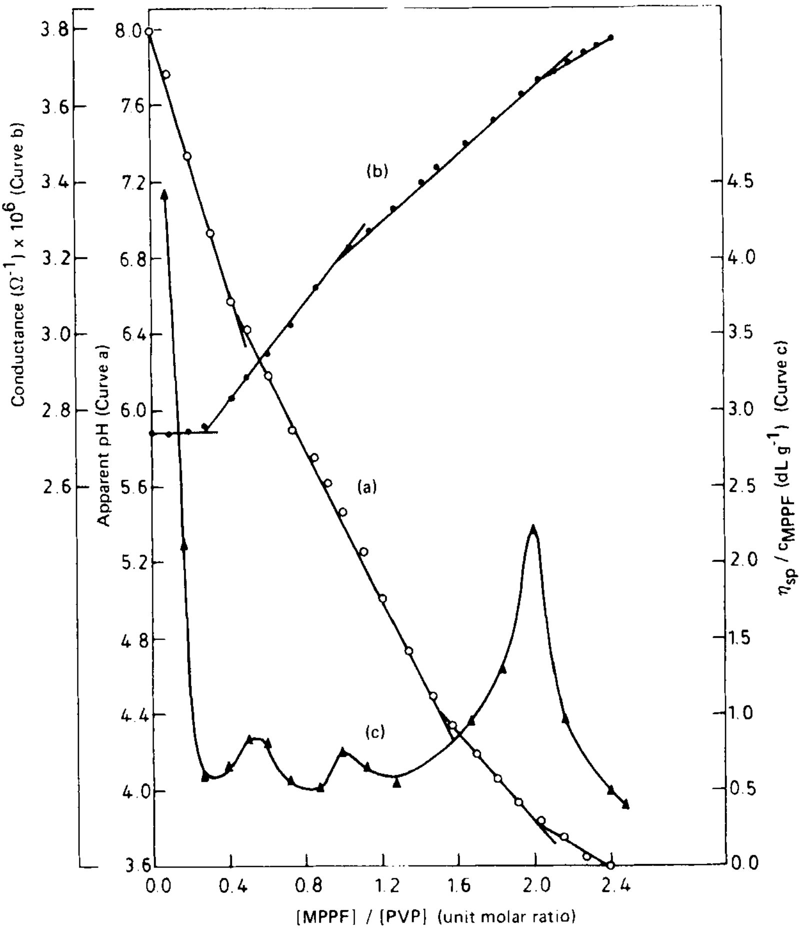


FIG. 1. Dependence of apparent pH, conductance, and reduced viscosity (η_{sp}/c_{MPPF}) with a unit molar ratio of MPPF and PVP: (a) apparent pH, (b) conductance, (c) reduced viscosity.

PVP, or may be due to hydrogen bonding with the carbonyl group of PVP. Of course, this process is expected to be noncooperative. However, the binding of a phenolic unit by at least three or four units in PVP chain may perturb the conformation of the interacting polymers (particularly PVP), which may result in the coiling up of the complex molecules. The abrupt fall in reduced viscosity on adding grafted copolymer to PVP may be attributed to this effect.

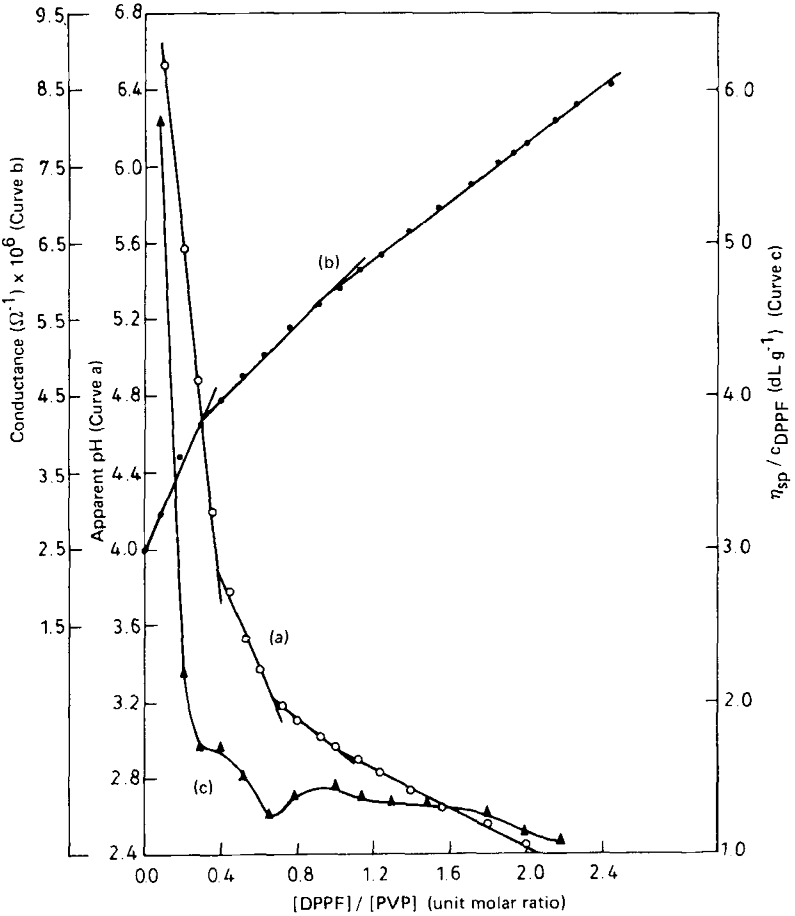


FIG. 2. Dependence of apparent pH, conductance, and reduced viscosity (η_{sp}/c_{DPPF}) with a unit molar ratio of DPPF and PVP: (a) apparent pH, (b) conductance, (c) reduced viscosity.

The general nature of the viscosity curve (e.g., Curve c of Figs. 1 to 3) during subsequent stages of interaction with PVP depends on the length of the grafted chain. In the case of monomer grafted copolymer (MPPF), three distinct maxima have been observed in the viscosity curve (e.g., Curve c of Fig. 1) at 0.5, 1.0, and 2.0 unit molar ratios (i.e., [MPPF]/[PVP]), whereas in the case of dimer and trimer grafted copolymers (i.e., DPPF and TPPF), only one maxima was observed at a 1:1 unit molar ratio (cf. Curve c of Figs.

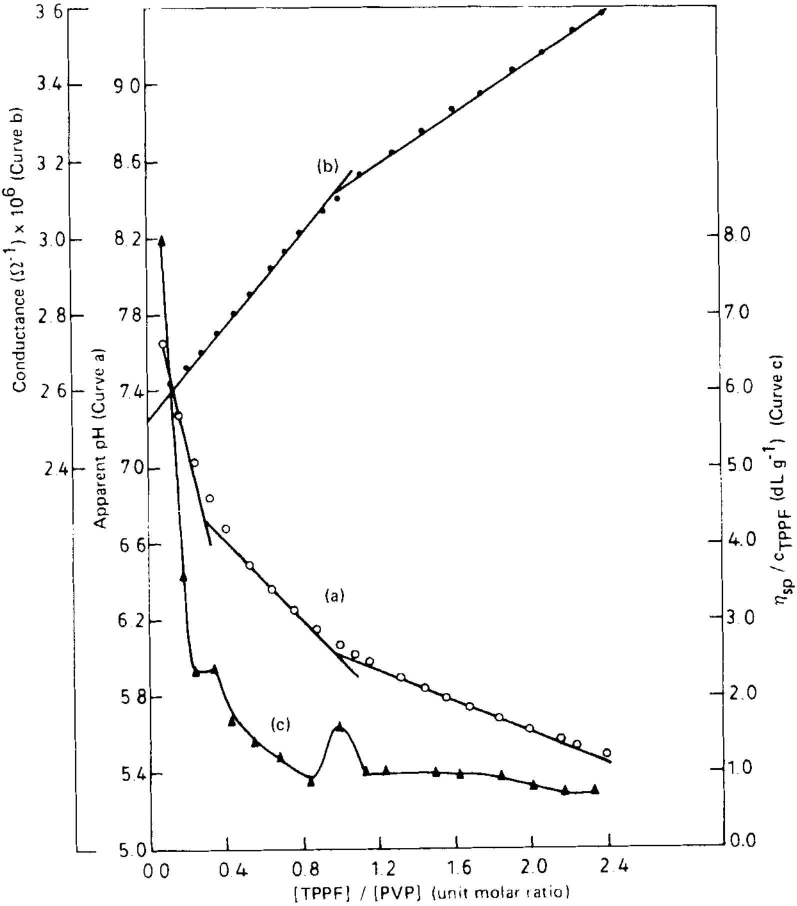
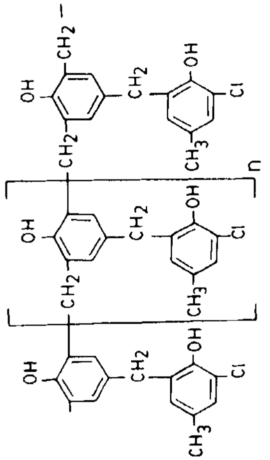


FIG. 3. Dependence of apparent pH, conductance, and reduced viscosity (η_{sp}/c_{TPPF}) with a unit molar ratio of TPPF and PVP: (a) apparent pH, (b) conductance, (c) reduced viscosity.

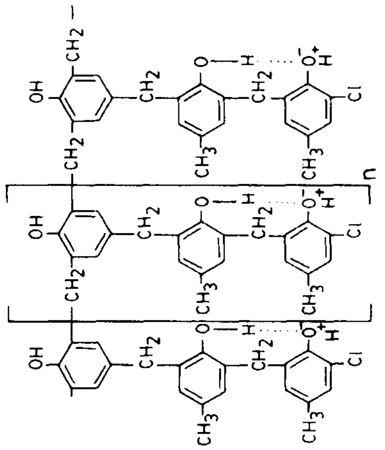
TABLE 1. Unit Molar Ratios Observed at Different Stages of Various Measurements

Interpolymer complex	pH	Conductance	η_{sp}/c
MPPF-PVP	-	0.25	0.25 (minima)
	0.5	1.0	0.5 (maxima)
	1.5	-	1.0 (maxima)
	2.0	2.0	2.0 (maxima)
DPPF-PVP	0.33	0.33	0.33 (minima)
	0.66	-	0.66 (minima)
	1.00	1.0	1.0 (maxima)
TPPF-PVP	0.3	-	0.3 (minima)
	-	-	0.85 (minima)
	1.0	1.0	1.0 (maxima)

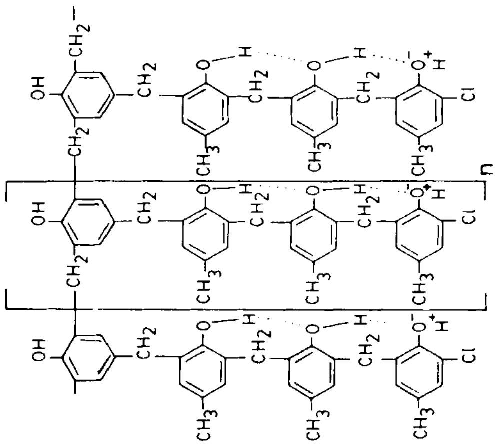
2 and 3). The basic structural difference between monomer, dimer, and trimer grafted copolymers is the presence of intramolecular H-bonding in the side chains of DPPF and TPPF, whereas the monomer units at the side chains of MPPF can be involved at the most in intermolecular H-bonding:



MPPF



DPPF



TPPF

Evidently intramolecular H-bonding is expected to be present in the main chains of all the copolymers. From the probable structure of the three graft copolymers (e.g., MPPF, DPPF, and TPFF), it is obvious that, compared to the phenolic units in DPPF and TPPF, phenolic units of MPPF will be more accessible to PVP units for interactions. As a result of interaction between PVP and MPPF at definite stoichiometries, (e.g., 0.5:1, 1:1, and 2:1), the complex may acquire some rigidity in its structure. This, in fact, is very well reflected by the three distinct maxima in its viscosity curve (cf. Curve c of Fig. 1), although, during the earlier stages of complexation of PVP with DPPF and TPPF, viscosity fell very abruptly due to the reasons mentioned earlier. In the subsequent stages of interaction, viscosity continued to fall and showed a weak maxima at a 1:1 unit molar ratio (cf. Curve c of Figs. 2 and 3). Thereafter the viscosity remained almost constant or fell very slowly. Since in DPPF and TPPF the length of the side chains are comparatively longer, it is therefore probable that some of the neighboring side chains may simultaneously interact with PVP units. As a result of this, one can expect the complex structure to become more and more compact till the unit molar ratio is unity. The continued fall in viscosity from 0.3 to 0.85 (unit molar ratio) could thus be anticipated. The distinct difference in behavior of the three graft copolymers during complexation with PVP can be attributed to the length of the grafted chains as well as to the presence of intramolecular H-bonding in the side chains in DPPF and TPPF. Unlike MPPF, DPPF and TPPF did not form any 2:1 (unit molar ratio) complex with PVP. This is obviously due to steric reasons, e.g., two phenolic units in the longer side chain may not be able to attach simultaneously with the tertiary N atom and the $-C{=}O$ group of the PVP unit. However, such a possibility does exist in the case of MPPF due to its comparatively more linear structure. In fact, the steep maxima observed in the viscosity curve of MPPF at 2:1 (unit molar ratio) indicates the formation of a complex with a reasonably rigid structure. Comparison of reduced viscosity values (η_{sp}/c) at 1:1 (unit molar ratio) for three graft copolymers indicated the following order: TPPF-PVP > DPPF-PVP > MPPF-PVP. This trend is expected in view of the indicated structure of the graft copolymers.

These interesting results could also be correlated by other independent method, e.g., conductance and apparent pH measurements at different stages of interaction of the graft copolymers with PVP. All the conductance curves (cf. Curve b of Figs. 1 to 3) showed an increase in conductance on adding graft copolymer to PVP, and distinct steps were observed at various stoichiometries (i.e., specific unit molar ratios of the components). Similarly, the pH curves (cf. Curve a of Figs. 1 to 3) indicated a steep fall in pH during the addition of graft copolymers to PVP, and most of the steps coincided (within experimental error) with the conductance and viscosity curves. The increase in conductance or the fall in pH during complexation probably indicates that the inter-

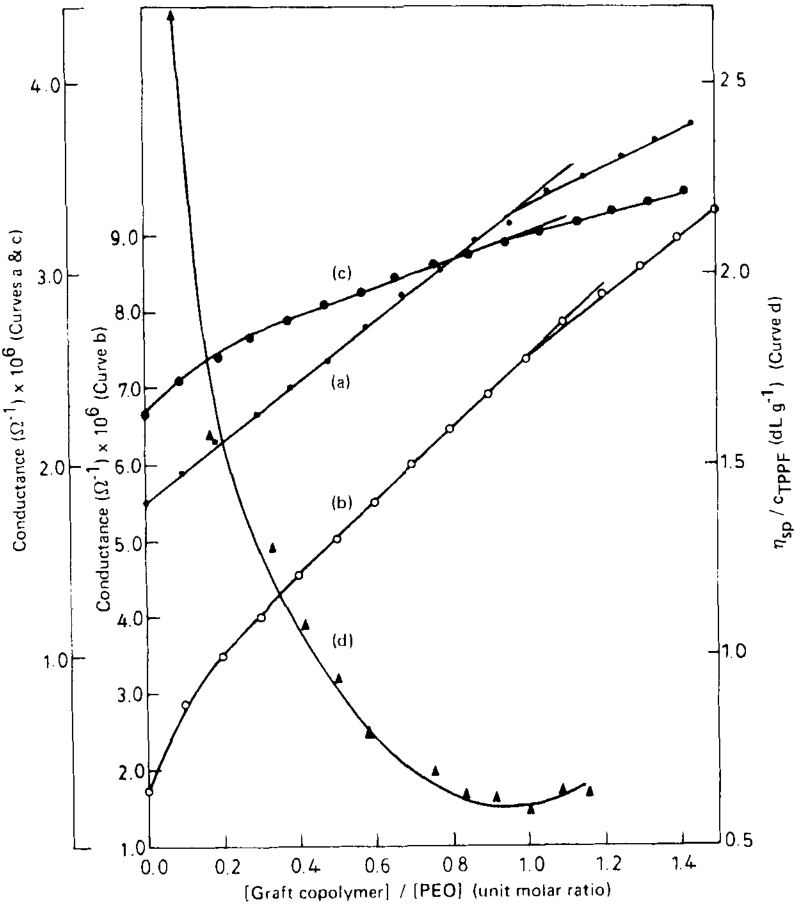


FIG. 4. Dependence of conductance (graft copolymer-PEO systems) and reduced viscosity with unit molar ratios of graft copolymer and PEO. Conductance: (a) MPPF-PEO, (b) DPPF-PEO, (c) TPPF-PEO, (d) reduced viscosity (η_{sp}/c_{TPPF}).

polymer complex is dissociating to some extent. This is expected in view of the fact that phenolic polymers in nonaqueous solvents behave as polyelectrolytes due to the presence of intramolecular H-bonding [3, 4]. The interpolymer complex formed as a result of proton transfer to the tertiary N-atom or by H-bonding through the carbonyl group may be in equilibrium with its dissociated species. Thus, the increase in conductance or fall in apparent pH during complexation of graft copolymers with PVP could possibly be accounted for. From the relative changes in conductance and apparent pH at various stages of complexation (cf. Curves b and a of Figs. 1 to 3), it is obvious that DPPF-PVP complex dissociated comparatively more than TPPF-PVP and MPPF-PVP complexes. It seems that both the factors e.g., intramolecular H-bonding in the side chains as well as its length, probably contribute to its dissociation. Comparison of the IR spectra of graft copolymers and its complexes made with PVP indicate a distinct shift of C–O bond stretching from 1225 to 1270 cm^{-1}, which clearly suggests involvement of OH groups of graft copolymers in interpolymer complex formation.

Further, it was interesting to see whether this distinct mode of complexation of grafted phenolic copolymers is unique with PVP or one could expect similar behavior with other nonionic copolymers. Keeping this fact in mind, complexation of the three graft copolymers has also been studied with another typical nonionic polymer, poly(ethylene oxide) (PEO). Some representative conductance and viscosity curves are shown in Fig. 4. Obviously, all the graft copolymers indicated only one type of complex, 1:1 (unit molar ratio). Incidentally, this behavior is identical with the interaction of PEO with polycarboxylic acids [2, 15].

These preliminary studies indicate that phenolic polymers, which find wide application in various industries, could possibly be used for more specific requirements by having them interact with suitably chosen nonionic homopolymers. Moreover, the length of the side chain of the graft copolymers seems to play a distinct role in the interaction between polymers.

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