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Interpolymer Complexes through Hydrophobic Interactions: C_{60}-End-Capped Linear or Four-Arm Poly(ethylene oxide)/Poly(acrylic acid) Complexes

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ABSTRACT: Complexation between C_{60}-end-capped linear or four-arm poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA) was studied. The introduction of hydrophobic [60]fullerene (C_{60}) in PEO has a dramatic effect on the complex formation of the PEO/PAA system. Interestingly, the yields of C_{60}-end-capped four-arm PEO/PAA complexes are lower than those of C_{60}-end-capped linear PEO/PAA complexes. The result indicates a competition between the hydrophobic effect and the steric effect originated from C_{60}. Similar to the PEO/PAA system, there are hydrogen-bonding interactions between the carboxylic acid groups of PAA and the ether oxygen in C_{60}-end-capped PEOs.

Introduction

When two dissimilar polymers are mixed in a common solvent, certain interpolymer interactions such as Coulombic, dipolar, hydrogen-bonding, and hydrophobic interactions can take place between the component polymers.[1−3] When interpolymer interaction outweighs polymer−solvent interaction, the two highly associated polymers precipitate out from the solution, and the precipitates are commonly called interpolymer complexes or simply complexes.[3]

Both poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) form intermolecular complexes with poly(ethylene oxide) (PEO) in dilute aqueous solutions through hydrogen-bonding interactions between carboxylic acid groups and ether oxygens of PEO. Because of the cooperative nature of interpolymer interaction, complexes do not form unless the chain lengths of the interacting polymers exceed a certain critical value. The critical degrees of polymerization of PEO for complexation with PAA and PMAA are about 200 and 40, respectively.[2,4,5] The smaller critical chain length for PMAA is attributed to the hydrophobic effect of its α-methyl groups. Hydrophobic interaction is caused by rearrangement of water molecules rather than direct cohesive force between the molecules, which forces the particles to coil up to into compact globules, thus stabilizing the polymer complex particles in water.

The complexation between PAA or PMAA and PEO substituted with a variety of hydrophobic groups such as naphthalene, 5-nitro-8-quinolinoxy, and 2-acteoxybenzonate groups has been studied by Rashkov and coworkers.[6−9] Anghel et al. also investigated the interactions between poly(ethylene glycol) monononylphenyl ethers and PAA.[10] These studies showed that the complexes originate from hydrogen bonding and are further stabilized by hydrophobic groups in the PEO chain. The complexation between PAA or PMAA and poly(vinyl ether) of ethylene glycol has also been studied.[11−14] Although the incorporation of hydrophobic comonomer units by copolymerization could disrupt the pairwise interpolymer interaction, the hydrophobic effect was found to enhance the stability of complexes.

[60]Fullerene (C_{60}) has received tremendous interest not only for its many promising applications but also for its unusual molecular structure and perfect spherical shape.[15−19] C_{60} is spherical with a diameter of about 1 nm and is highly hydrophobic. Because of its large three-dimensional structure, it is very interesting to study the hydrophobic effect of C_{60} on the complexation between poly(carboxylic acid)s and poly(ethylene oxide)s. In a previous paper, we reported that the end-capping of PEO with hydrophobic C_{60} has a dramatic effect on the complex formation of the PEO/PMAA system.[20] The yield of the precipitated complex can reach as high as 92% when both ends of PEO are capped with C_{60}. In the present paper we report the hydrophobic effect of C_{60} on the complexation between PEO and PAA.

Experimental Section

C_{60} (99.9% pure) was obtained from Peking University, China. PAA with a reported viscosity-average molecular weight (M_v) of 450 000 was obtained from Aldrich; PMAA (reported $M_v = 400\ 000$) was obtained from Polysciences, Inc. Three PEOs were obtained from Aldrich; their number-average molecular weight (M_n)/polydispersity values are 2500/1.07 (PEO2), 5000/1.06 (PEO5), and 10 000/1.06 (PEO10), respectively. Four-arm PEO (4APEO) was obtained from Polymer Source, Inc.; its M_n and polydispersity are 7400 and 1.06, respectively.

C_{60}-end-capped PEOs (FPEO2F, FPEO5F, FPEO10F, and F4APEOF) were prepared using the same method as the synthesis of single-C_{60}-end-capped PEO as reported previously.[21] Basically, the hydroxyl groups of PEO were converted to chlorine groups through reaction with thionyl chloride. The chloro-terminated PEO was then reacted with sodium azide to form azido-terminated PEO which subsequently underwent cycloaddition reaction with C_{60} to afford C_{60}-end-caped PEO (Scheme 1).

Various polymers were dissolved in water (1% w/v) separately. Appropriate amounts of the aqueous solutions were then mixed. For C_{60}-end-capped linear PEOs, precipitates formed immediately upon mixing the two solutions. The mixtures were stirred continuously for 24 h to ensure equilibrium was attained. For star-shaped F4APEOF, precipitation occurred gradually, and the mixtures were stirred continuously at 500 rpm for 84 h. The complex in a form of precipitates

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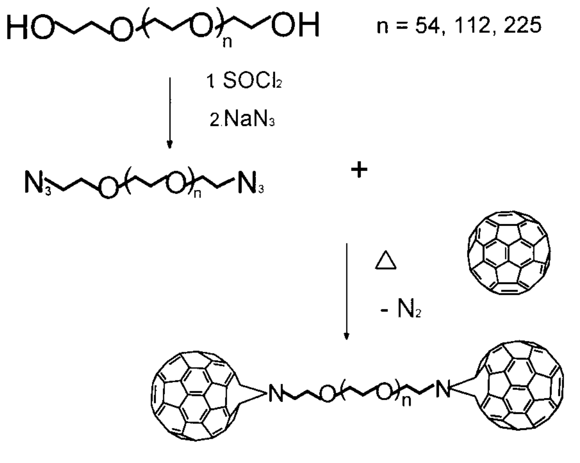
Scheme 1



was isolated by centrifugation, washed with water, and then dried in vacuo at 60 °C for 1 week. The ratio of the amount of dried complex to the total weight of two polymers in the initial solutions gives the yield of the complex. When the mixing of two aqueous solutions did not lead to precipitation, the solution was evaporated to dryness. The resulting film was designated as a polymer blend. The polymer blends were also dried in vacuo at 60 °C for 1 week.

The glass transition temperature (T_g) values of various complexes and blends were measured using a TA Instruments 2920 differential scanning calorimeter. T_g's of samples were taken from the second heating scan as the extrapolated onset point of the abrupt increase in heat capacity in DSC curve. Thermogravimetric measurements were made with a TA Instruments SDT 2960 simultaneous DTA−TGA. About 8 mg of sample was heated at 5 °C/min from room temperature to 1000 °C in a dynamic nitrogen atmosphere (flow rate = 50 mL/min). FTIR spectra were acquired using a Bio-Rad 165 FTIR spectrophotometer. All spectra were recorded at 105 °C to exclude moisture; 32 scans were signal-averaged at a resolution of 2 cm^{-1}.

X-ray photoelectron spectroscopic (XPS) measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Various samples were ground to fine powders and then mounted on standard sample studs by means of a double-sided adhesive tape. The X-ray source was run at 12 kV and 10 mA. A pass energy of 20 eV and a rate of 0.05 eV/step were used for all the high-resolution XPS spectra acquisition with a binding energy width of 12 eV. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during the measurements. All spectra were obtained at a takeoff angle of 75° and were curve-fitted with XPSPEAK3.1.

Results and Discussion

Figure 1 shows the XPS spectra of FPEO5F, FPEO10F, and F4APEOF. The C 1s spectra show the existence of two different states of carbon in the C_{60}-end-capped PEOs. The low-binding-energy (BE) peaks are centered at 284.6 eV, corresponding to the carbon of C_{60}. The high-BE peaks are centered at about 286.2 eV, corresponding to the carbon in PEO chain. The electron-withdrawing effect of oxygen makes the PEO carbon electron-deficient, leading to a higher BE. From peak area measurements, the low-BE peaks represent 32, 20, and 41% of all carbon, which agree well with the theoretical values of 35, 21, and 42% for FPEO5F, FPEO10F, and F4APEOF respectively, assuming quantitative reaction and monoaddition. Accordingly, the majority of the C_{60} in F4APEOF, FPEO10F, and FPEO5F are attached to a single PEO chain.

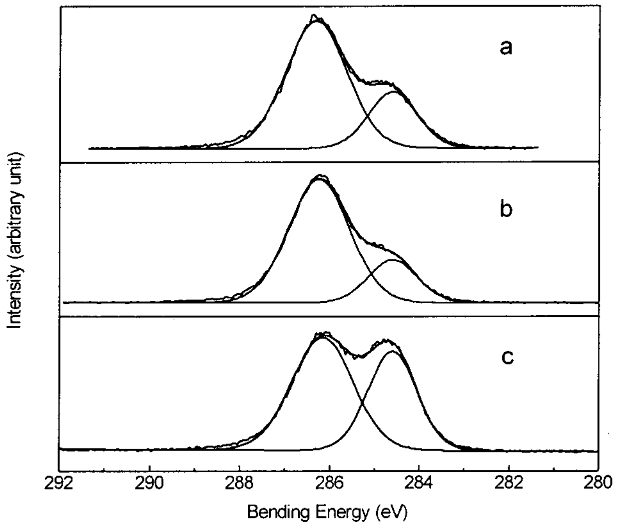


Figure 1. C 1s spectra of FPEO5F, FPEO10F, and F4APEOF.

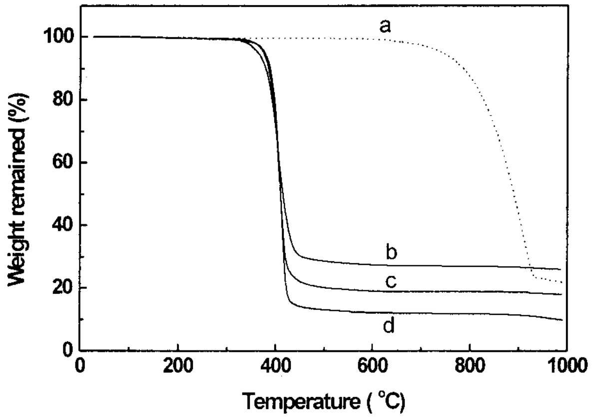


Figure 2. TG curves of (a) pristine C_{60} (dash line), (b) F4APEOF, (c) FPEO5F, and (d) FPEO10F.

Figure 2 shows the thermogravimetric (TG) curves of pristine C_{60}, F4APEOF, FPEO5F, and FPEO10F. C_{60} is thermally stable below 600 °C, and PEO decomposes completely by 400 °C. The amount of C_{60} incorporated into the polymer chain could then be estimated by TG.[22] The weights remained at 500 °C of F4APEOF, FPEO5F, and FPEO10F are about 27, 20, and 12 wt %, which agree well with the theoretical values of 28.0, 22.4, and 12.6 wt %, respectively, assuming monoaddition between azido-teminated PEOs and C_{60}. Therefore, both XPS and TG results suggest that the C_{60}-end-capped PEOs samples mainly consist of monoadduct.

The mixing of the aqueous solutions of 4APEO and PAA led to a slightly milky solution. Precipitates could not be isolated after standing and centrifugation. The solutions were then evaporated to dryness to give 4APEO/PAA blends. Similarly, the mixing of the aqueous solutions of PEO2, PEO5, and PEO10 with PAA also only led to slightly milky solutions. In contrast, precipitation occurred when the aqueous solution of PAA was mixed with those of C_{60}-end-capped PEOs. The yields of various complexes are given in Table 1. The yield of FPEO10F/PAA complex is 72% when FPEO10F and PAA were mixed in a feed ratio of $^4/_6$. PEO end-capped with the other organic hydrophobic groups such as naphthalene, as mentioned earlier, does not form precipitates when mixed with PAA.[6−9] Apparently, the hydrophobic effect of C_{60} is stronger than those of the other organic substituents. The steric effect arising from

Table 1. Yields of Complexes

PAA in feed (wt %)	FPEO2F (%)	FPEO5F (%)	FPEO10F (%)	F4APEOF (%)
20	15	13	13	1 (1)[a]
40	40	38	40	14 (15)
50	59	53	55	18 (34)
60	56	57	72	33 (27)
80	25	31	45	2 (4)

[a] Value in parentheses represents yield of F4APEOF/PMAA complex.

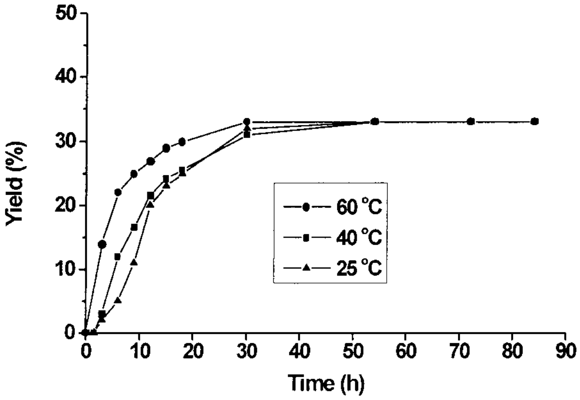


Figure 3. Yield of F4APEOF/PAA complex (using a feed ratio of $^4/_6$) as a function of time.

the bulkiness of C_{60} could prevent a close association between the two dissimilar polymers. However, since the C_{60}-end-capped linear PEO forms complexes more readily than the correcoponding PEO, the hydrophobic effect of C_{60} plays a more important role. It is worthy to note that for C_{60}-end-capped linear PEO, the yield of the complex is relatively independent of the chain length of PEO. However, the yields of the complexes are lower than those of the corresponding FPEOF/PMAA complexes which can reach as high as 92%.[20] The higher yields of the PMAA complexes also demonstrate the hydrophobic effect of the α-methyl groups in PMAA.

Interestingly, the yields of PAA/F4APEOF complexes are lower than those of the C_{60}-end-capped linear PEOs. The average molecular weight of each PEO arm in F4APEOF is 1850. Using the following empirical relationship of Devanand and Selser[23] for PEO in water, the hydrodynamic radius R_H of the PEO branch is roughly 1 nm.

$$R_H/\text{Å} = 0.145 M_w^{0.571\pm0.009}$$

Therefore, the four C_{60} entities in F4APEOF are quite close to each other, and thus the steric effect created by C_{60} becomes significant, leading to a low yield of complex. The results imply that there is a competition between the hydrophobic effect and the steric effect originated from C_{60}. It was observed that, for linear FPEOFs, precipitates formed immediately upon mixing the two solutions, but for F4APEOF, precipitation occurred slowly. The slow precipitation of the F4APEOF/PAA complexes offers another evidence of the steric effect of C_{60}. Figure 3 shows that the yield of an F4APEOF/PAA complex (using a feed ratio of $^4/_6$) increases with time at different temperatures. The higher the temperature, the faster the precipitation is. At 60 °C, a small amount of complex precipitates appeared immediately upon mixing the solutions. The high mobility of the PEO chains at high-temperature facilitates the formation of complex. However, the yield of complex is independent of temperature, reaching 33% at equilibrium. It is noted that the yields of the F4APEOF/PAA complexes are about the same as those of the F4APEOF/PMAA complexes (Table 1), showing that the hydrophobic effect of the α-methyl groups in PMAA becomes insignificant when the four-arm PEO is overcrowded with C_{60}.

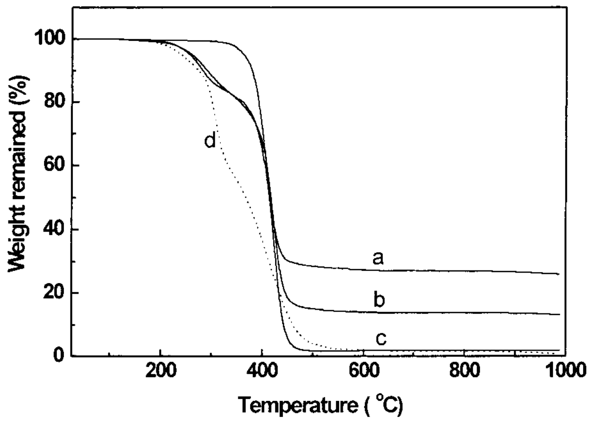


Figure 4. TG curves of (a) F4APEOF, (b) F4APEOF/PAA, (c) 4APEO/PAA, and (d) PAA (dash line).

Table 2. Compositions of F4APEOF/PAA Complexes

F4APEOF in feed (wt %)	20	40	50	60	80
F4APEOF in complex (wt %)	*a*	54	57	61	*a*
EO/AA molar ratio in complex	*a*	1.4	1.6	1.8	*a*

[a] Yield of complex is too low to allow characterization.

Table 3. Compositions of FPEO2F/PAA Complexes

FPEO2F in feed (wt %)	20	40	50	60	80
FPEO2F in complex (wt %)	46	55	56	57	69
EO/AA molar ratio in complex	0.9	1.3	1.3	1.4	2.3

Table 4. Compositions of FPEO5F/PAA Complexes

FPEO5F in feed (wt %)	20	40	50	60	80
FPEO5F in complex (wt %)	47	54	57	59	67
EO/AA molar ratio in complex	1.1	1.5	1.7	1.8	2.6

Table 5. Compositions of FPEO10F/PAA Complexes

FPEO10F in feed (wt %)	20	40	50	60	80
FPEO10F in complex (wt %)	49	55	59	61	69
EO/AA molar ratio in complex	1.4	1.7	2.1	2.2	3.2

The compositions of various complexes can be estimated by thermogravimetry (TG). The TG curves of F4APEOF, PAA, F4APEOF/PAA complex (obtained from a feed ratio of $^4/_6$) and 4APEO/PAA ($^4/_6$) blend are shown in Figure 4. The blend is almost completely decomposed by 500 °C. It can be assumed that for the F4APEOF/PAA complexes the weights remained above 500 °C are due to the C_{60} core. On this basis, the compositions of F4APEOF/PAA complexes were estimated, and the results are shown in Table 2. The compositions other complexes of C_{60}-end-capped linear PEOs and PAA were similarly estimated, and the results are shown in Tables 3–5. The yield and composition of complex depend on feed composition as commonly observed for many interpolymer complexes.[24–31] The EO/AA ratio in the complex increases with increasing C_{60}-end-capped PEO content in the feed.

Figure 5 shows the FTIR spectra of PAA and the FPEO5F/PAA complexes. PAA is predominantly self-associated as an intermolecular hydrogen-bonded dimer characterized by a strong carbonyl stretching band

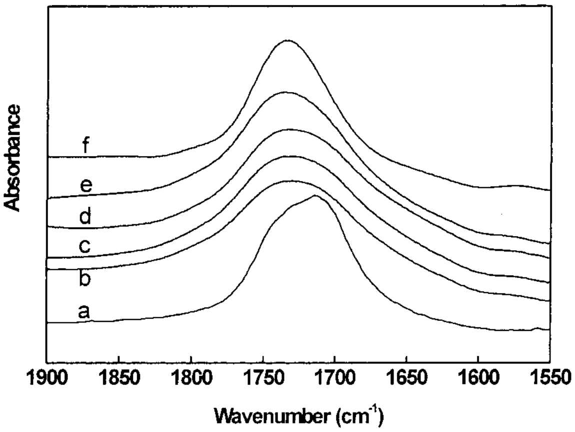


Figure 5. FTIR spectra of the carbonyl stretching region of (a) PAA and FPEO5F/PAA complexes prepared from feed ratios of (b) 20/80, (c) 40/60, (d) 50/50, (e) 60/40, and (f) 80/20.

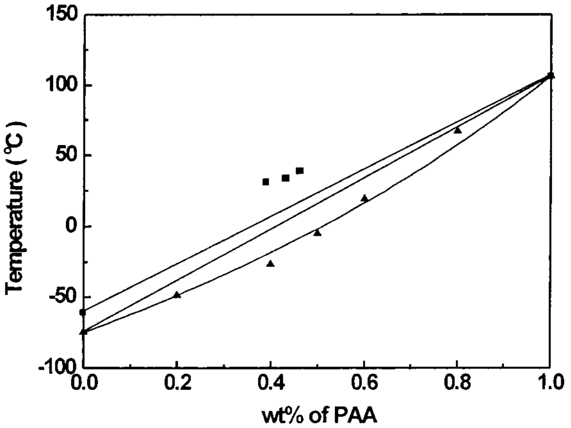


Figure 6. T_g values of 4APEO/PAA blends (▲) and F4APEOF/PAA complexes (■). The straight line gives the T_g value calculated from a linear additivity rule.

around 1710 cm^{-1}.[24] However, the peak maxima of the complexes are located at 1734 cm^{-1} and become more intense with increasing FPEO5F content in the complex. The results show that most of the self-association in PAA has been replaced by intermolecular hydrogen bonding involving the carboxylic acid groups and the ether oxygens of FPEO5F. The spectra of other complexes also show similar features as the FPEO5F/PAA complexes.

As mentioned earlier, two polymers coprecipitate to form a complex when polymer−polymer interaction outweighs polymer−solvent interaction. It is commonly observed that the T_g value of a complex is higher than that predicted by a linear additivity rule using the T_g values of the component polymers.[24−31] The close contact between dissimilar polymers reduces segmental mobility and thus increases the T_g value. As shown in Figure 6, the T_g values of the 4APEO/PAA blends are lower than those predicted by the linear additivity rule. In contrast, the T_g values of the F4APEOF/PAA complexes are higher than those predicted by the additivity rule, suggesting a more compact nature of the complexes. Figure 7 compares the T_g values of various linear FPEOF/PAA complexes and PEO5/PAA blends. Similarly, the T_g values of the complexes are in general higher than the predicted values based on the linear additivity rule.

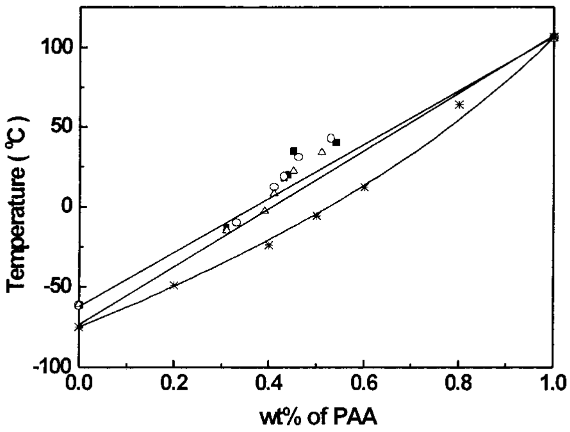


Figure 7. T_g values of PEO5/PAA blends (*), FPEO2F/PAA complexes (■), FPEO5F/PAA complexes (○), and FPEO10F/PAA complexes (△). The straight line gives the T_g value calculated from a linear additivity rule.

Conclusion

The introduction of hydrophobic C_{60} in linear PEOs has a dramatic effect on the complex formation of the PEO/PAA system. The yield of FPEO10F/PAA complex can reach as high as 72%. Interestingly, the yields of four-arm F4APEOF/PAA complexes are relatively low, suggesting a competition between the hydrophobic effect and the steric effect originated from C_{60} during complexation with PAA in aqueous solution. Similar to the PEO/PAA system, there are hydrogen-bonding interactions between the carboxylic acid groups of PAA and the ether oxygen in C_{60}-end-capped PEOs.

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