Interpolymer Complexes through Hydrophobic Interactions: C_{60}-End-Capped Poly(ethylene oxide)/Poly(methacrylic acid) Complexes

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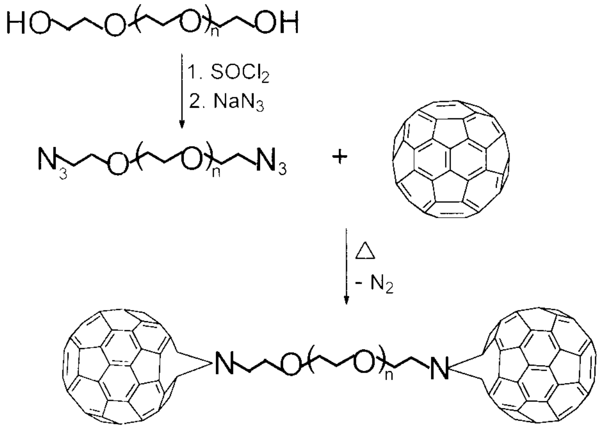
Introduction

Interpolymer complexation is an intermolecular association of two different polymers through secondary binding forces.[1] The intermolecular association between different polymers in solution is evidenced by a reduction in viscosity arising from a highly compact nature of the associated polymer chains. When the intermolecular interaction between polymers outweighs the polymer−solvent interaction, the two highly associated polymers precipitate out from the solution, and the precipitates are commonly called interpolymer complexes or complexes. Therefore, the formation of precipitates upon mixing two polymer solutions in a common solvent indicates the presence of strong interpolymer interaction. On the basis of the dominating interaction forces, interpolymer complexes can be divided into several classes: polyelectrolyte complexes, which are formed by mixing oppositely charged polyelectrolytes, i.e., polyanions and polycations, due to Coulombic forces; hydrogen-bonding complexes, which are stabilized through hydrogen bonds between a polyacid and a polybase; charge-transfer complexes, which are formed between polymers with electron-donor and electron-acceptor groups; stereocomplexes which are typically formed through van der Waals forces by two polymers with identical chemical structure and complementary stereoisomerism. Polyelectrolyte complexes and hydrogen-bonding complexes have received the most attention.[2−14] In addition, interpolymer complexes may be stabilized by other interactions such as hydrophobic interaction in aqueous solution.[1] Hydrophobic force is different from the others because hydrophobic interaction is caused by rearrangement of water molecules rather than direct cohesive force between the molecules. Hydrophobic interaction forces the particles to coil up into compact globules, playing an essential role in the stabilization of the polymer complex particles in water.

Poly(methacrylic acid) (PMAA) forms an interpolymer complex with poly(ethylene oxide) (PEO) in dilute aqueous solutions through hydrogen-bonding interactions between carboxylic acid groups of PMAA and ether oxygens of PEO.[1,15] Moreover, the PMAA/PEO complex is also stabilized by hydrophobic interaction due to the hydrophobic α-methyl groups as evidenced by a smaller critical chain length for complexation of PMAA than that of poly(acrylic acid) (PAA).[15] Rashkov and coworkers[16−19] studied the complexation between PMAA and PEO substituted with a variety of hydrophobic groups such as naphthalene, 5-nitro-8-quinolinoxy, and 2-acetoxybenzoate groups and found that the stability of the complexes was greatly enhanced as shown by viscosity measurements. In all cases, the two polymers did not precipitate out from the solution. In general, the more hydrophobic the substituent, the more stable the complex is.

Scheme 1



[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.[20,21] C_{60}-containing polymers are the subject of several recent reviews.[22−24] 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 PMAA and PEO. It will be shown that PEO forms complexes with PMAA more readily when one or both ends of PEO are capped with C_{60}.

Experimental Section

C_{60} (99.9% pure) was obtained from Peking University, China. PMAA ($M_v = 400\,000$) was obtained from Polysciences, Inc. Two poly(ethylene glycol) monomethyl ether (PEO) samples were obtained from Aldrich; their M_n/polydispersity values are 2200/1.07 (PEO1) and 5100/1.08 (PEO2), respectively, determined by GPC. Poly(ethylene glycol) was obtained from Aldrich; its M_n and polydispersity are 2500 and 1.07, respectively.

Single-C_{60}-end-capped poly(ethylene oxide) (FPEO) was prepared by cycloaddition reaction of monoazido-terminated poly(ethylene oxide) (starting from PEO1) with C_{60}.[25] Double-C_{60}-end-capped poly(ethylene oxide) (FPEOF) was prepared following same procedure as FPEO, using poly(ethylene glycol) with M_n of 2500 as the starting material (Scheme 1). The molecular structures of PEO, FPEO, and FPEOF are shown in Scheme 2.

Various polymers were dissolved in water (1% w/v) separately. Appropriate amounts of aqueous solutions were then mixed. In the case where precipitation occurred, the complex in a form of precipitates 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

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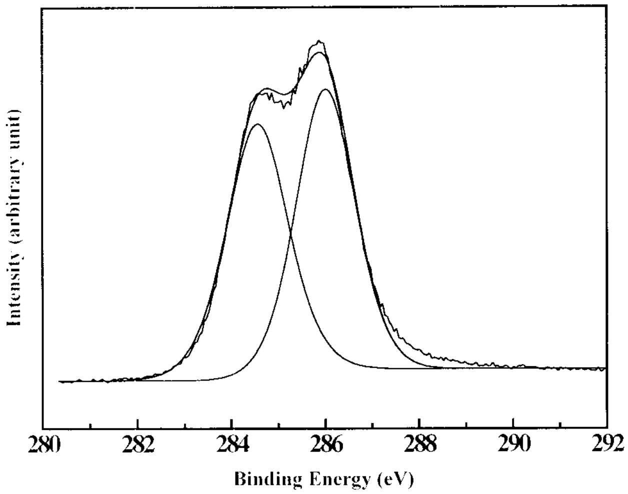
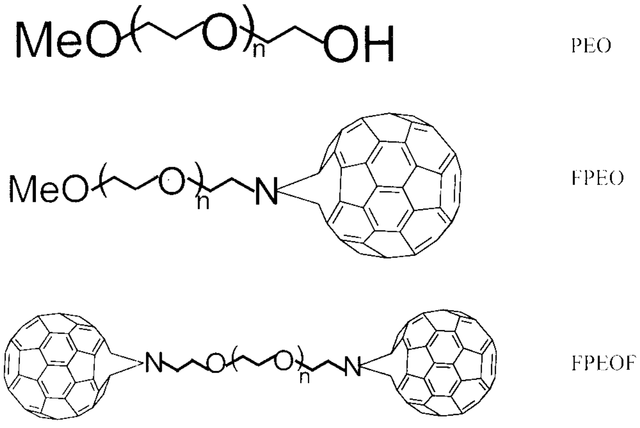


Figure 1. C 1s spectrum of FPEOF.

Scheme 2



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. 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 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 spectrum of FPEOF. The C 1s spectrum shows the existence of two different states of carbon in FPEOF. The low-binding-energy (BE) peak is centered at 284.6 eV, corresponding to the carbon of C_{60}. The high-BE peak is centered at 286.0 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 peak represents 49% of all carbon, which agrees well with the theoretical value of 51% assuming quantitative reaction and monoaddition. We have earlier reported that there is an average of 1.1 PEO chains per C_{60} molecule for FPEO based on XPS measurements.[25] Therefore, the majority of the C_{60} in FPEO and FPEOF are attached to a single PEO chain.

Table 1. Yields of PEO/PMAA, FPEO/PMAA, and FPEOF/PMAA Complexes

PMAA in feed (wt %)	PEO1 (%)	PEO2 (%)	FPEO (%)	FPEOF (%)
20	0	4	4	4
40	0	11	5	23
50	0	5	6	92
60	0	2	11	49
80	0	0	5	32

The yields of various complexes are summarized in Table 1. In all cases, the mixing of PEO1 and PMAA aqueous solutions led to a milky solution. Precipitates could not be isolated after standing and centrifugation. The solutions were then evaporated to dryness to give PEO1/PMAA blends. The mixing of PEO2 and PMAA solutions also led to a milky solution. However, small amounts of precipitates could be isolated in four cases. Because of the cooperative nature of complexation, complex cannot form when chain lengths of the two polymers are smaller than a critical value.[1,15] Apparently, the higher molecular weight of PEO2 facilitates complexation with PMAA.

The yield of complex increases when one or both chain ends of PEO are capped with C_{60}. When PEO1 is end-capped with C_{60}, the resulting FPEO forms a complex with PMAA more readily. The yields of FPEO/PMAA complexes are comparable to those of PEO2/PMAA complexes although the chain length of PEO2 is twice that of the PEO in FPEO. For FPEOF in which both ends are capped with C_{60}, the effect is more dramatic. When FPEOF and PMAA were mixed in equal weight ratio, the yield of complex reached 92%. The supernatant liquid was colorless even though the original FPEOF solution was dark red, indicating that nearly all the FPEOF had precipitated. As mentioned earlier, PMAA does not form precipitates with PEO end-capped with hydrophobic groups such as naphthalene.[16−19] Thus, the formation of precipitates between PMAA and FPEO or FPEOF clearly demonstrates that the hydrophobic effect of C_{60} is far more superior than those of the other organic substituents.

The compositions of various complexes can be estimated by thermogravimetry (TG). C_{60} is stable below 600 °C. The TG curves of the FPEOF, PMAA, FPEOF/PMAA complex (obtained from a feed ratio of 1/1) and the PEO1/PMAA blend (1/1) are shown in Figure 2. The blend almost completely decomposed by 500 °C. It can be assumed that for the FPEOF/PMAA complexes the weights remained above 500 °C are due to the C_{60} core. On this basis, the compositions of FPEOF/PMAA complexes are estimated, and the results are shown in Table 2. The yield and composition of the complex depend on the feed composition as commonly observed for many interpolymer complexes.[2−7,11−13] The EO/MAA ratio in the complexes increases with increasing FPEOF content in the feed.

Figure 3 shows the FTIR spectra of PMAA and the FPEOF/PMAA complexes. PMAA is strongly self-as-

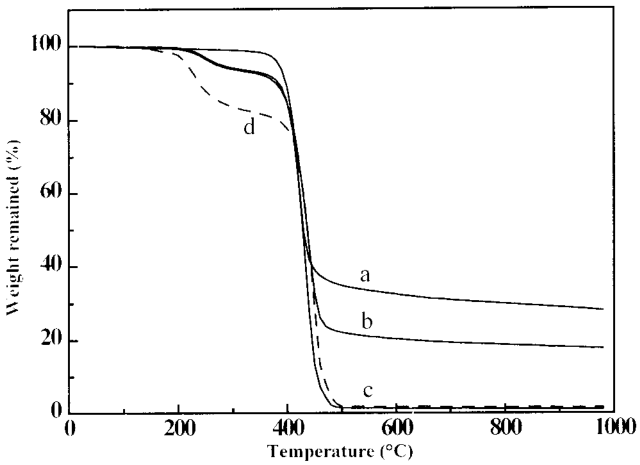


Figure 2. TG curves of (a) FPEOF, (b) FPEOF/PMAA complex (50/50), (c) PEO1/PMAA blend (50/50), and (d) PMAA (dash line).

Table 2. Compositions of FPEOF/PMAA Complexes

FPEOF in feed (wt %)	20	40	50	60	80
FPEOF in complex (wt %)	40	51	59	68	71
EO/MAA molar ratio in complex	0.8	1.3	1.8	2.7	3.1

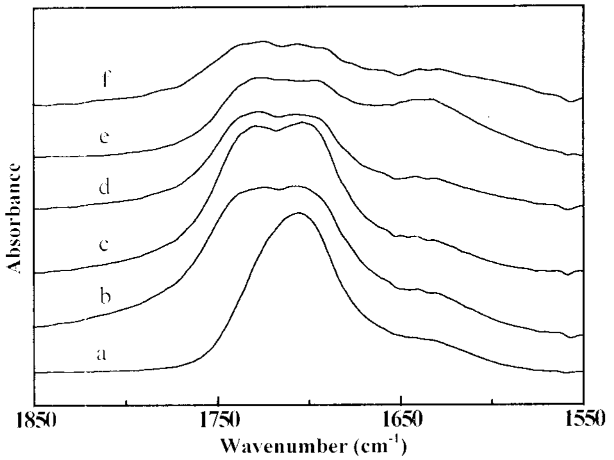


Figure 3. FTIR spectra of the carbonyl stretching region of FPEOF/PMAA complexes of different feed ratio (a) 0/100, (b) 20/80, (c) 40/60, (d) 50/50, (e) 60/40, and (f) 80/20.

sociated through characteristic intermolecular hydrogen-bonded dimer and has a strong carbonyl band at 1700 cm^{-1}.[26] However, in the FPEOF/PMAA complexes, a new band at 1728 cm^{-1} appears. The new band is assigned to liberated "free" carbonyl groups when an intermolecular interaction (hydrogen bond) is formed between the carboxylic acid group of MAA and the ether oxygen atom of FPEOF. This observation is the same as that reported for the PEO/PMAA system.[26]

All the PEO1/PMAA blends cast from water show a single T_g, indicating miscibility. The T_g–composition curve of the blends can be correlated by the Kwei equation:[27]

$$T_g = [(w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)] + qw_1w_2$$

where T_g, T_{g1}, and T_{g2} are respectively the glass transition temperature of the blend, polymer 1, and polymer 2; w_1 and w_2 are the corresponding weight fractions; and k and q are fitting constants. The q value is assumed to be proportional to the number of specific interactions between the two polymers.[27] As shown in Figure 4, the

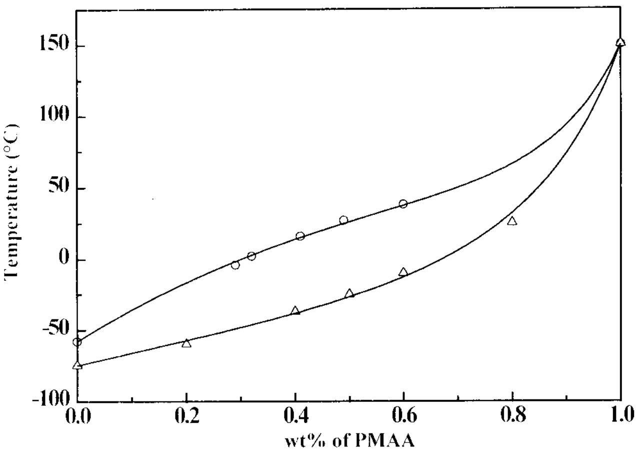


Figure 4. T_g–composition curves for FPEOF/PMAA complexes (○, $k = 0.2$, $q = 200$) and PEO1/PMAA blends (△, $k = 0.2$, $q = 40$).

T_g–composition curve for PEO1/PMAA blends can be fitted using $k = 0.2$ and $q = 40$. Each of the FPEOF/PMAA complexes also shows only one T_g, and the T_g–composition curve can also be fitted by the Kwei equation, using $k = 0.2$ and $q = 200$. The q values appear to suggest that the interaction between FPEOF and PMAA is more intense than that between PEO1 and PMAA, resulting in a more compact structure and a higher T_g of the FPEOF/PMAA complex. This implication is consistent with the conclusion from a fluorescence study by Oyama et al.[28,29] on PEO/PMAA and PEO/PAA complexes in aqueous solutions. The hydrophobicity of PMAA arising form the α-methyl groups creates a more compact and rigid structure upon complexation with PEO in aqueous solutions than observed for PAA.

Conclusion

The introduction of hydrophobic C_{60} in PEO has a dramatic effect on the complex formation of the PEO/PMAA system. The yield of FPEOF/PMAA complex can reach as high as 92%. Similar to the PEO/PMAA system, there are hydrogen-bonding interactions between the carboxylic acid groups of PMAA and the ether oxygens in FPEOF.

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