Bull. Chem. Soc. Jpn., 69, 473—476 (1996)

Anomalous Formation of Ion Conducting Polymer-Networks in Polymer Films

Takayuki Ohta* **and Shiho Sano**

Research Center, Mitsubishi Chemical Corporation, Kamoshida, Yokohama 227

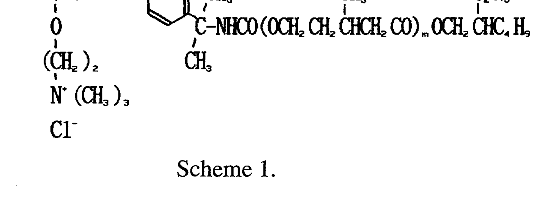
(Received June 28, 1995)

An amphiphilic graft-copolymer consisting of ionic segments (quaternary ammonium groups) and aliphatic polyester segments which are compatible with various polymers was synthesized by radical copolymerization of a (methacryloxyethyl)trimethylammonium chloride and a poly(β-methyl-δ-valerolactone) macromer. Polymer blends containing this graft-copolymer showed both low surface resistance and low volume resistivity, due to the network formation of the graft-copolymer in the polymer matrix. Scanning electron microscopy revealed that the graft copolymer forms interconnected granular aggregates, which function as ion-conducting channels.

Electrons can pass through metallic powders and fibers of Cu, Ag, carbon black, and conducting organic polymers such as polyaniline and polythiophene,[1)] while ions can pass through some types of metal oxides[2)] and metal complexes with poly(ethylene oxide).[3)] When these electron- and ion-conducting substances are mixed with polymers, the electron- and ion-conductivities are enhanced, probably by the formation of electron conducting channels. However, these electron-conducting channels have been observed by transmission electron microscopy only in a specific polymer blend system,[4)] and has not been well understood in other systems.[5)] Here we report an anomalous formation of ion-conducting polymer-networks in polymer blend films, which has been visually caught by scanning electron microscopy (SEM). This was discovered in the course of our study on synthesis and properties of a novel graft-copolymer (Scheme 1) as a polymeric antistatic agent.[6)] The graft-copolymer is amphiphilic and consists of ionic segments (quaternary ammonium groups) and aliphatic polyester segments which are compatible with various polymers.

Experimental

Materials. All solvents, monomers, and other chemicals used in this work were purchased from commercial suppliers and purified by conventional methods. (Methacryloxyethyl)trimethylammonium chloride (MAC) was purchased from Nitto Chemical Industry Co. and used as such. Poly(methylmetacrylate) (PMMA) with $M_n = 4.7 \times 10^4$ daltons was purchased from Mitsubishi Rayon Co. and used as such.



Scheme 1.

Synthesis of Polyester Macromer (PMV Macromer). PMV macromer was synthesized by two steps which involve the syntheses of polyesters having a hydroxyl group at one end (PMVH) and PMV macromers.

At first, PMVH, poly(β-methyl-δ-valerolactone), was prepared by ring-opening polymerization of β-methyl-δ-valerolactone (MVL), and then reacted with *m*-isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI) according to the method reported previously.[6,7)]

Synthesis of Graft Copolymer (PMAC-g-PMV). In a 200 ml flask fitted with a gas-inlet, 10 g of the polyester macromer, 10 g of (methacryloxyethyl)trimethylammonium chloride (MAC), 0.2 g of AIBN, 0.4 g of 1-dodecanethiol, and 40 ml of 2-propanol (IPA) were heated to polymerize at 70 °C for 7 h under stirring. After an additional heating at 95 °C for 2 h, the reaction mixture was poured into an excess amount of a mixture of IPA and heptane (1/4 by weight) to remove the unreacted macromer and to precipitate the product. This was filtered off, washed with the same solvent mixture, and dried in vacuo at room temperature. It was characterized by ^{1}H and ^{13}C NMR spectroscopies and GPC (column, Shodex Asahipak GS-7MHQ; solvent, methanol; detector, multi-angle light scattering detector from Wyatt Technology).

SEM Micrographs. For morphology study by SEM, a blend film composed of PMAC-g-PMV (20 wt%) and PMMA (80 wt%) was prepared by casting their solution in a mixture of ethyl methyl ketone and methanol (80/20 by wt%). The film was soaked in a 5% aqueous solution of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ for 24 h at ambient temperature in order to fix the morphology of the graft-copolymer. It was then washed with water, and dried in an oven. The blend film was then immersed in toluene for more than 24 h at ambient temperature to extract PMMA from it (PMMA is soluble in toluene while PMAC-g-PMV is not). The residue thus obtained was dried, overcoated with gold, and subjected to SEM.

The blend film, without being treated with any aqueous ammonium heptamolybdate, was immersed for more than 24 h in methanol to extract PMAC-g-PMV (which is soluble in methanol while

PMMA is not) and subjected to SEM as mentioned above.

Measurement of Surface Resistance and Volume Resistivity. A typical sample for the measurement was obtained as follows. PMAC-g-PMV and PMMA were dissolved in appropriate solvent systems such as a mixture of ethyl methyl ketone and methanol. The resulting solution was cast on a polyethylene sheet and dried at 70 °C in a drying oven. The obtained film was kept at 23 °C and 50% RH for 48 h before the measurement, which was conducted by using a high resistance meter produced by Yokogawa-Hewlett-Packard.

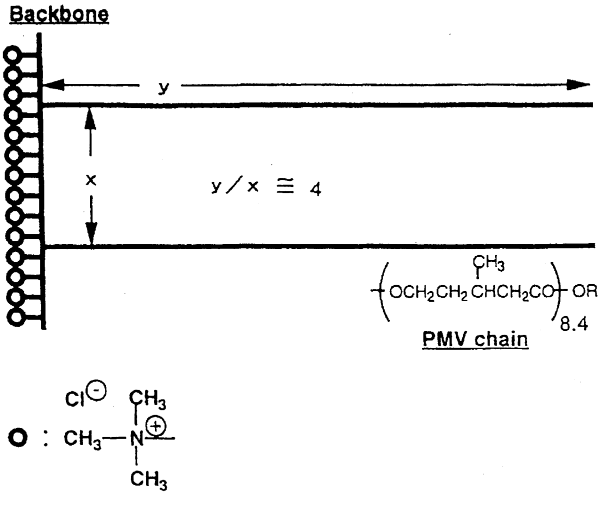
Results and Discussion

PMVH prepared by ring-opening polymerization of MVL was a colorless viscous liquid at room temperature; its hydroxyl value was 58.6 KOH mg/g. M_n and M_w/M_n of PMVH by GPC were 1260 daltons and 1.77, respectively.

The bulk reaction of PMVH with *m*-TMI yielded PMV macromer with $M_n = 1400$ daltons and $M_w/M_n = 2.08$; it was a colorless viscous liquid at room temperature. Its GPC curve detected by UV represented the introduction of aromatic groups coming from *m*-TMI. This result combined with its ^{1}H and ^{13}C NMR spectra supported the formation of the isopropenylphenyl-terminated poly(β-methyl-δ-valerolactone) macromer.[6,7)]

The graft-copolymer (PMAC-g-PMV) was synthesized by radical copolymerization of PMV macromer prepared above and (methacryloxyethyl)trimethylammonium chloride. The inherent viscosity of PMAC-g-PMV was 0.15 dl/g (0.5 g/dl, methanol), and its M_n and M_w/M_n were 7500 daltons and 10.9, respectively, as measured by GPC. PMAC-g-PMV was white hygroscopic powder, soluble in alcoholic solvents such as methanol and ethanol, but almost insoluble in THF and water. It was characterized by ^{1}H and ^{13}C NMR spectra and can be depicted as shown in Scheme 2.[7)]

PMAC-g-PMV is amphiphilic, possessing both the aliphatic polyester segments which are compatible with matrix polymers and the ionic segments. The polymer blends of PMAC-g-PMV can afford a very low surface resistance and a transparent coating with excellent antistatic properties. Of particular interest was the result that the volume resistivities of the blend film comprising PMAC-g-PMV and such matrix polymers as PMMA, poly(vinyl chloride), and polyurethane were very low, 10^8—10^9 ohms·cm. On the other hand, a film of pure PMMA used as a matrix polymer showed a resistivity higher than 10^{15} ohms·cm.[6,7)] These facts suggest that the polyblend may have an unusual structure and morphology.



Scheme 2. Schematic structure of PMAC-g-PMV.

Figure 1 shows the SEM micrographs of the extracted film. Here the brighter regions indicate the structure of PMAC-g-PMV which remained as the insoluble residue by the toluene extraction, and the darker regions are voids that were occupied by the matrix polymer PMMA before the extraction (PMAC-g-PMV is soluble in methanol and not in toluene. PMMA is soluble in toluene and not in methanol). This result indicates that the PMAC-g-PMV network is constructed by fine particles interconnected with each other. As shown in Fig. 2(a), a number of holes formed by the extraction of PMAC-g-PMV with methanol were observed on the surface

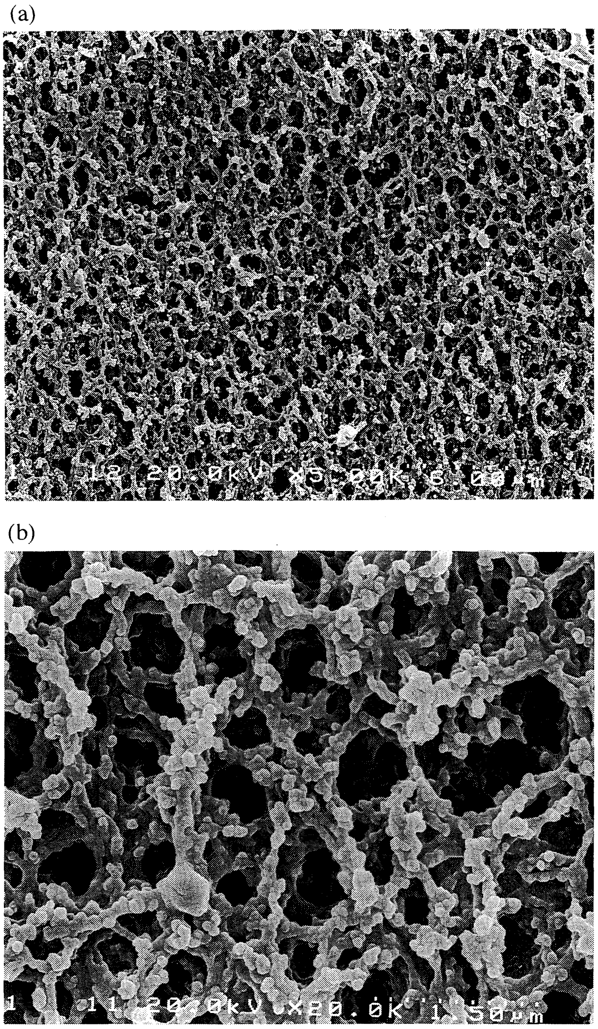


Fig. 1. SEM micrographs of PMAC-g-PMV (20 wt%) blended PMMA film extracted with toluene at two different magnifications. These micrographs show the networks of interconnected granular PMAC-g-PMV aggregates formed inside the PMMA matrix.

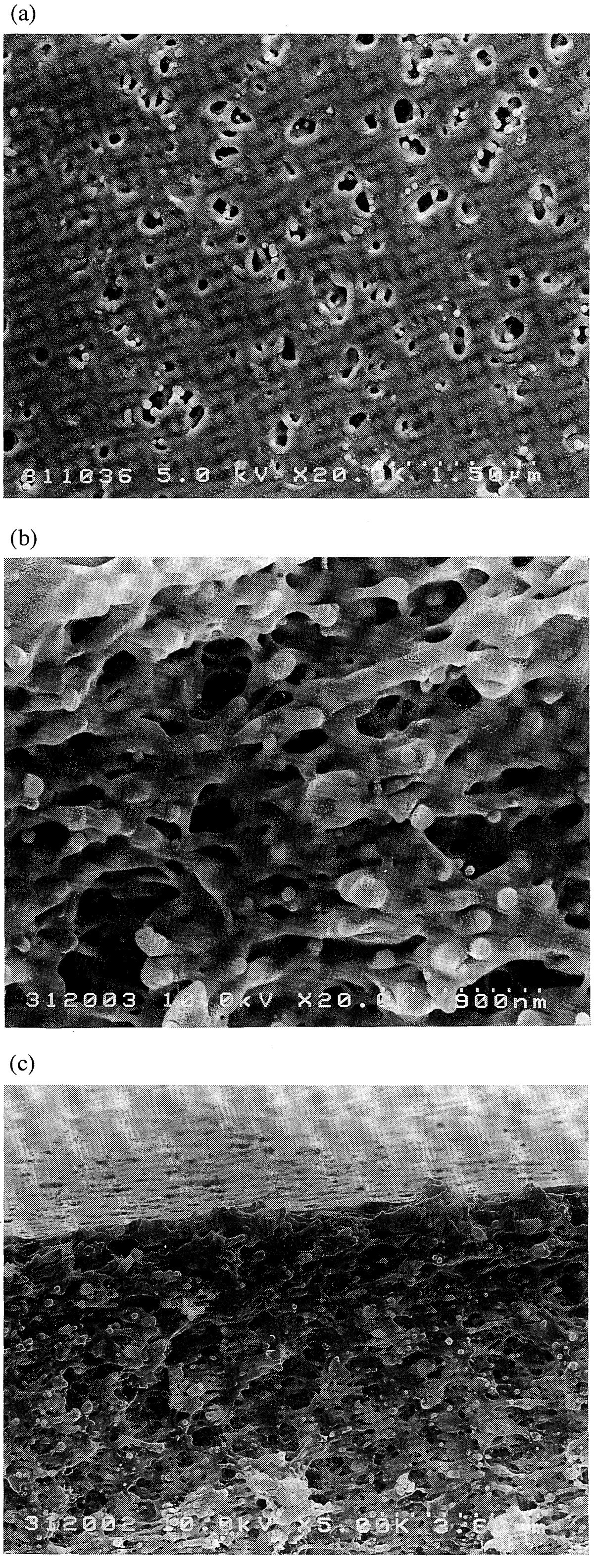


Fig. 2. SEM micrographs of PMAC-g-PMV (20 wt%) blended PMMA film extracted with methanol. These micrographs display a number of holes and numerous cavities formed by the extraction of PMAC-g-PMV with methanol. (a); surface, (b); cross section, (c); surface and cross section.

of the film. This structure is quite opposite to the former. Figure 2(b) shows the numerous cavities formed inside the film. These are shown more clearly in Fig. 2(c), which was taken for the surface and cross section of the film.

Analyses of the SEM micrographs of Figs. 1 and 2 suggested the following mechanism for the formation of the PMAC-g-PMV networks. In the course of drying of the cast solution, the concentration of PMAC-g-PMV increases, and PMAC-g-PMV gradually deposits out of the solution in a form of fine particles, which are stabilized by the PMV grafts and compatible with the PMMA. These particles aggregate with each other to form the interconnected networks. The driving force for the formation of these aggregates and networks is considered to be the ionic interaction of the quaternary ammonium groups of the PMAC segments. Therefore, the inner part of the aggregates may consist mainly of the quaternary ammonium salts, which act as the ion conducting channels. The outer part may be composed mainly of the PMV segments to increase compatibility with the matrix. This morphology, with the ionic networks inside the film, is the origin of the low volume resistivity.

However, we can not exclude the possibility that the networks of PMAC-g-PMV are formed by spinodal decomposition following phase separation.

By blending only 5—10 wt% of PMAC-g-PMV the volume resistivity became as low as 10^8—10^9 ohms·cm; this is very significant in terms of applications. The blend film pretreated with the aqueous ammonium heptamolybdate dissolved completely in toluene and no network structure remained. However, formation of the ionic interconnected pathways may be an essential structure for the graft-copolymer to decrease the resistivity at its extremely low compositions.

The ionic interactions between the quaternary ammonium groups should not be so strong, because the immersion of the PMAC-g-PMV (20 wt%) blended PMMA film in toluene without pretreating with the aqueous ammonium heptamolybdate resulted in complete loss of the structure, just like the pure PMMA film. Therefore, the ammonium heptamolybdate worked as a very important cross-linking agent for PMAC-g-PMV to fix its morphology. Addition of a small amount of the aqueous ammonium heptamolybdate to the PMAC-g-PMV solution in methanol brought about white precipitates. The cross-linking is based on the following ion exchange reactions:

$$\begin{aligned}
&\mathrm{P[{-}COOC_2H_4N(CH_3)_3Cl]}_x + \mathrm{(NH_4)_6Mo_7O_{24}}\\
&\rightarrow \mathrm{P[{-}COOC_2H_4N(CH_3)_3Cl]}_{x-1}\\
&\qquad \mathrm{[{-}COOC_2H_4N(CH_3)_3](NH_4)_5Mo_7O_{24}} + \mathrm{NH_4Cl}\\
&\rightarrow \mathrm{P[{-}COOC_2H_4N(CH_3)_3Cl]}_{x-y}\\
&\qquad \mathrm{[{-}COOC_2H_4N(CH_3)_3]}_y\mathrm{(NH_4)}_{6-y}\mathrm{Mo_7O_{24}} + y\mathrm{NH_4Cl}
\end{aligned}$$

P; polymer chain

Conclusion

The micrographs of the blend film extracted with toluene, originally comprising the graft-copolymer PMAC-g-

PMV and PMMA, revealed that the networks are formed by aggregation of phase-separated small particles of PMAC-g-PMV, which function as ion conducting channels to afford the low volume resistivity. This was accomplished by a combination of this type of graft-copolymer and the first use of the aqueous ammonium heptamolybdate as a staining agent.

Kenji Mori is thanked for his help with the SEM micrographs.

References

1) J. E. Frommer and R. R. Chance, "Encyclopedia of Polymer Science and Engineering," 2nd ed, J. Wiley & Sons, New York (1985), Vol. 15, pp. 462—507.

2) O. Nakamura, T. Komada, I. Ogino, and Y. Miyake, *Chem. Lett.*, **1979**, 17.

3) W. M. Allan, A. Hooper, and R. A. Pethrick, *Eur. Polym. J.*, **25**, 1297 (1989).

4) C. Y. Yang, Y. Cao, P. Smith, and A. J. Heeger, *Synth. Met.*, **53**, 293 (1993).

5) C. K. Subramaniam, A. B. Kaiser, P. W. Gilberd, and B. Wessling, *J. Polym. Sci.*, *Part B*, *Polym. Phys.*, **31**, 1425 (1993); B.-L. Lee, *Soc. Plast. Eng.*, (*Tech. Pap.*), **38**, 474 (1992).

6) T. Ohta, S. Sano, J. Goto, and A. Kasai, *Polym. Prepr.*, *Am. Chem. Soc.*, *Div. Polym. Chem.*, **34**, 590 (1993).

7) T. Ohta, S. Sano, J. Goto, and A. Kasai, *New Polymer Materials*, in press.