Morphologies of Poly(vinylcarbazole)–Polyisoprene Graft Copolymer and Blend

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SYNOPSIS

The microstructures of a poly(vinylcarbazole-g-isoprene) and blend of poly(vinylcarbazole) (PVCz) and polyisoprene (PIP) were studied by transmission electron microscopy (TEM). In the graft copolymer, the unique microphase separated structure was observed. In the blend, the blend ratio did not correspond to the area ratio on the TEM photograph. It is suggested that the results are caused by rigid and crystalline PVCz and low glass-transition temperature of PIP. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that block and graft copolymers that consist of two amorphous sequences generally form a micelle in solvent over critical micelle concentration. During the solvent evaporation, the micelle deforms and a final microphase separated structure is fixed. This structure principally consists of five morphologies.[1] Especially graft copolymer, which is synthesized more easily than block copolymers, is applied in the preparation of high functional polymer materials.[2–4] If one sequence consists of a functional polymer with special electrical properties, the graft copolymer film consists of many ordered microdomains with the electrical characteristic and may show different electrical properties in comparison with the film consisting of only the homopolymer. However, in order to form a well ordered microstructure, well defined graft copolymer is needed. In a preceding article, well defined poly(vinylcarbazole-g-isoprene) (PVCz-g-IP) graft copolymers were synthesized in order to achieve this purpose.

Poly(vinylcarbazole) (PVCz) is used as a photoconducting polymer. The microstructure of the graft copolymer is the photoconducting microdomain separated by an insulator domain.

In this work, the microstructure of the PVCz-g-IP was studied by transmission electron microscopy (TEM). In order to compare the microstructure of the graft copolymer with the blend of each homopolymer, the same study by TEM was carried out at various blend ratios and solvents.

EXPERIMENTAL

Synthesis of PVCz-g-IP

PVCz-g-IP was synthesized by the reaction between partially chloromethylated PVCz and living polyisoprene (PIP) monoanion (described in preceding paper[5]). Each homopolymer was used for the blend. The characteristics of the polymer are listed in Table I.
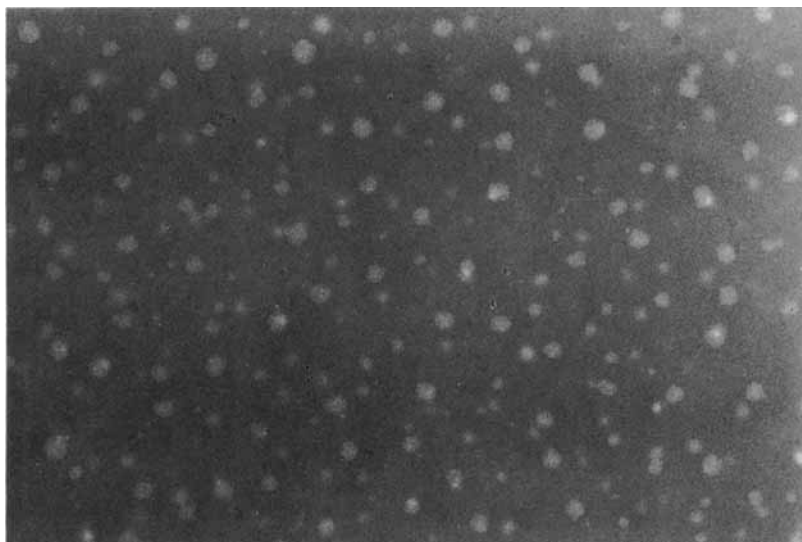
Electron Microscopy

The graft copolymer and blend were dissolved in tetrahydrofuran (THF, good for both sequences) or a THF/n-hexane mixture (good for PIP and poor for PVCz). The blend ratio and solvent are listed in Table II. The solution was deposited on copper mesh covered with carbon film. The solvent was evaporated in atmospheric pressure at room tem-
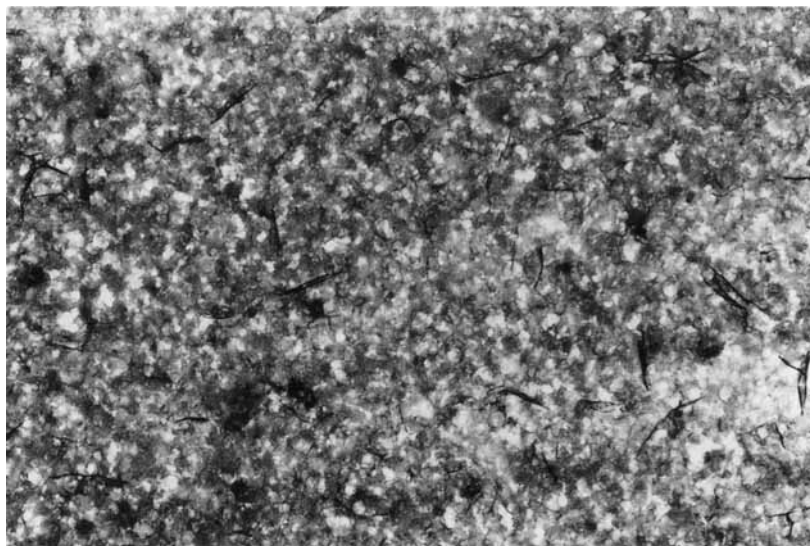
200 nm

(a)

500 nm

(b)

Figure 1   TEM photographs of G1 and G2. Dark areas are PIP domains. (a) G1 and (b) G2.

perature. After the evaporation, the specimen was dried in vacuum for 5 days and the PIP domain was stained with osmium tetraoxide. The TEM observations were carried out on a Hitachi H-500 model with an acceleration voltage of 100 kV.

RESULTS AND DISCUSSION

Figure 1 shows the TEM photographs of G1 and G2. The white area is the PVCz domain. In G1, a unique microstructure is observed; PVCz domains are ir-

Table I Characteristics of Homopolymers and Graft Copolymers

Polymer	$M_w \times 10^{-4}$ PVCz	PIP (1 Chain)	Brunches Number (Per 1 PVCz Chain)
HomoPVCz	9.3		
HomoPIP		1.1	
Poly(VCz-g-IP)	9.3	3.6 (1.1)	3.3

M_w measured by GPC universal calibration. Brunches number measured by NMR.

regular spheres whose domain size is less than 100 nm. By Molau's rule, the microdomain structure of block and graft copolymers are determined by the volume fraction in the solution. The volume fraction of graft copolymer in THF is unknown because the solvent–polymer (THF–PVCz and THF–PIP) interaction is unknown. But the microstructure should be a PIP cylinder or alternate lamellar structure considering that the weight and mol fraction of PVCz are 72 wt % and 48 mol %, respectively. The densities of PVCz and PIP are 0.988 and 0.925 g/cm^3, respectively,[6] and THF is a good solvent for
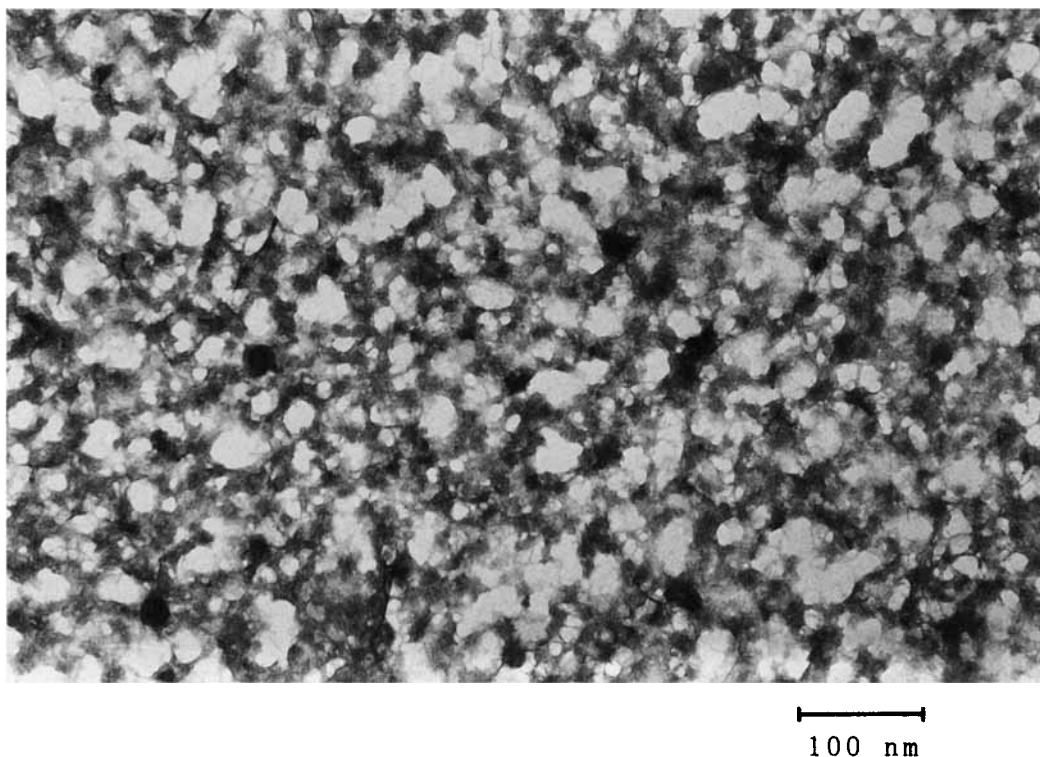
Table II Characteristics of Specimens

| Run No.[a]	Composition wt % PVCz	wt % PIP	mol % PVCz	mol % PIP	Casting Solvent
G1	72	28	48	52	THF
G2	72	28	48	52	Mixture[b]
B1	50	50	26	74	THF
B2	87	13	70	30	THF
B3	24	76	10	90	THF
B4	13	87	5	95	THF
B5	50	50	26	74	Mixture[b]
B6	24	76	10	90	Mixture[b]

[a] G1 and G2: PVCz-g-IP. B1–B6: blend of PVCz and PIP.
[b] THF/n-hexane (8 : 2 vol).

both sequences. However, the observed structure is not the usual sphere, cylinder, and lamellar structure. It was reported that PVCz is a rigid polymer because of the bulky carbazole group.[7,8] PVCz is a crystalline polymer. In preceding studies, the microstructure of the crystalline-amorphous type block copolymer was different from that of the amorphous-amorphous type because of the crystallization. And

100 nm

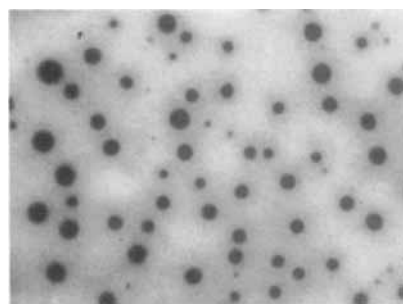**Figure 2** TEM photograph magnified for Figure 1(a).

1 μ m
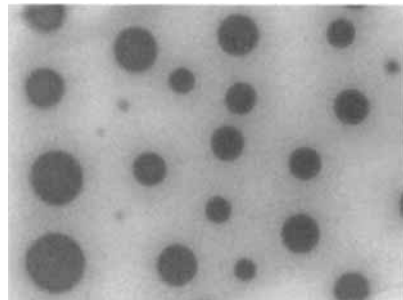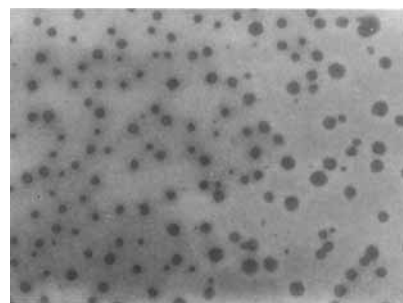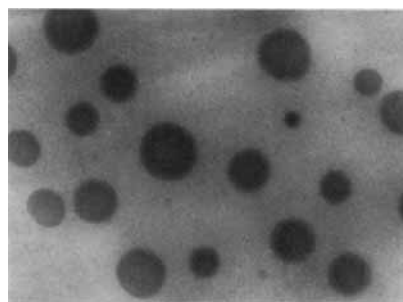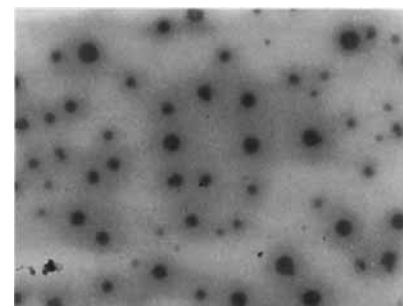

(a)
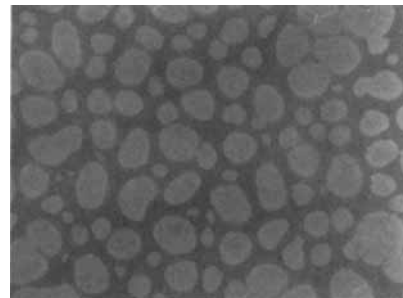
(b)

(c)

(d)

(e)

(f)

Figure 3   TEM photographs of B1–B6 specimens. Dark areas are PIP domains. (a) B1; (b) B2; (c) B3; (d) B4; (e) B5; (f) B6.

Table III Domain Characteristics of Graft Copolymer and Blend

Run No.	Domain Shape	Domain Size[a] (nm)	Area Ratio of PVCz Domain (%)
G1	Microphase separation[b]	—[c]	—[b]
G2	PVCz sphere	57	11
B1	PIP sphere	306	68
B2	PVCz disc	—	52
B3	PIP sphere	122	92
B4	PIP sphere	103	88
B5	PIP sphere	267	82
B6	PIP sphere	117	92

(—) Not measurable.

[a] Diameter of sphere.

[b] This shape is an ordinary microphase separation for domain size. But the shape is not assigned to Molau's five morphologies. PIP domain is incorporated in PVCz domain.

then, the degree of freedom for PVCz is small because the PVCz chain is a main chain not a graft chain. For these reasons, the microstructure in G1 became the unique structure. In this structure, it is suggested that the PVCz chain cannot be packed uniformly in the PVCz domain or the PIP chain is incorporated into the PVCz domain. Figure 2 shows the magnified Figure 1(a). There are many black lines in the PVCz domains (white part). It is suggested that these lines correspond to incorporated PIP chains.

In G2, PVCz spheres are observed [Figure 1(b)]. In this specimen, because the solvent is good for PIP and poor for PVCz, the volume fraction of PVCz became small. This structure is reasonable considering Molau's rule.[1]

Figure 3 shows the TEM photographs of B1–B6 specimens. Table III lists the domain characteristics of all specimens. In the blend specimens, the domain shapes are PIP spheres except for B2. The domain sizes of B3, B4, and B6 are about double that of G1 and G2, and small in comparison with that of usual blend polymers. The domain shapes do not correspond to the volume fraction. In B3, B4, and B6, the area ratios of PVCz is large (about 90%); however, the PIP fractions are small. The domain structure of B3 almost agrees with that of B6 although the casting solvent was different. On the other hand, in the graft copolymer, the solvent effect for the domain structure was clearly recognized. In B1 and B5, the area ratio of PVCz is different (casting solvent was different). In only B2 the disk structure of PVCz is observed. From these results, even if the

PVCz fraction is small, the area ratio of PVCz is not small. By considering the crystalline and rigid PVCz, and the low glass-transition temperature (T_g) of PIP,[6] the domain structure may not correspond to the blend ratio. In crystalline-amorphous type block copolymer, such a discrepancy caused by the crystallization was reported.[9] Because blend polymer does not have a junction of both sequences like block copolymer, the discrepancy is apt to occur.

From these results, the microstructures of graft copolymer or blend containing the PVCz chain in these thin films were different from those of the usual amorphous graft copolymers or blends.

CONCLUSIONS

The microstructure of the PVCz-g-IP and blend of PVCz and PIP were studied by using of TEM observations. In the graft copolymer (PVCz = 48 mol %), the unique microphase separation was observed. This structure was caused by the rigid and crystalline PVCz chain. In the blend, the blend ratio did not correspond to the area ratio on the TEM photographs. Especially, when the PVCz fraction was small, the area ratio was not small. It is suggested that because PVCz is a rigid and crystalline polymer, the discrepancy between the volume fraction and area ratio occur. The microstructures of graft copolymer or blend containing PVCz chain in these thin films were different from the usual amorphous graft copolymers or blends.

REFERENCES

1. G. E. Molau, *Block Copolymers*, S. L. Aggarwal, Ed., Plenum, New York, 1970, p. 79.
2. P. J. F. Kanitz and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **15**, 67 (1971).
3. P. Aptel, N. Challard, and J. Neel, *J. Membrane Sci.*, **1**, 271 (1976).
4. B. G. Ranby, *J. Polym. Sci., Polym. Symp.*, **51**, 89 (1975).
5. S. Ishikawa, *Makromol. Chem.*, to appear.
6. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley-Interscience, New York, 1975.
7. J. Hughes and A. M. North, *Trans. Farad. Soc.*, **62**, 1866 (1966).
8. S. Yoshimoto, Y. Akana, A. Kimura, S. Kusabayashi, and H. Mikawa, *Chem. Commun.*, **1969**, 987 (1969).
9. A. Takahashi and Y. Yamashita, *Copolymers, Polyblends, and Composites*, A. J. Platzer, Ed., Am. Chem. Soc., Washington DC, 1975, p. 267.