

Some Unusual Properties of Graft Copolymers and Polyblends of β -Vinyl-naphthalene and Ethylene Oxide*

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Synopsis

It was found that poly- β -vinyl-naphthalene and poly(ethylene oxide) (54:46% by weight) form homogeneous blends or graft copolymers when prepared under conditions which inhibit the crystallization of poly(ethylene oxide). Such preparations can be obtained from solutions in a good solvent for both components, either by precipitation procedures which lead to coacervation rather than fractionation, or by freeze-drying. Preparations containing more than 46 wt.-% poly(ethylene oxide) were characterized by modulus versus temperature curves exhibiting a minimum at about 60°C. This behavior was interpreted as due to microphase separation taking place with increasing temperature, a process which becomes irreversible above 120°C. A graft copolymer having the 54:46 composition was rubbery at room temperature, and in contrast to polyblends did not exhibit the poly- β -vinyl-naphthalene glass transition at 138°C. The marked difference in behavior between polyblends and graft copolymers is due to the fact that in the latter irreversible microphase separation cannot take place. The above described properties seem to be peculiar to poly- β -vinyl-naphthalene. Similar properties could not be reproduced in preparations of poly(ethylene oxide) with polystyrene, poly-4-vinylbiphenyl, or polyacenaphthylene. These preparations exhibited a behavior characteristic of mixtures of two incompatible polymers.

Introduction

A method recently developed for the synthesis of graft copolymers of vinyl aromatic polymers and polyethylene oxide^{1,2} offers possibilities for the preparation of materials which combine the properties of two incompatible polymers. In order to evaluate the spectrum of properties that can be obtained, a study was made of both blends and grafts of these polymers. In particular, the system composed of poly- β -vinyl-naphthalene and poly(ethylene oxide) was emphasized as it was found that these materials can achieve limited compatibility under certain conditions. This property was manifest in modulus versus temperature curves exhibiting a minimum as well as the formation of a graft copolymer having rubbery properties at room temperature. Similar behavior could not be observed for systems containing polystyrene or poly-4-vinylbiphenyl.

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Experimental

Two batches of poly- β -vinylnaphthalene (PVN) were prepared by emulsion polymerization and had molecular weights of 510,000 and 720,000 which were used for the blends and grafts, respectively. Both polystyrene (PS, $M_w = 150,000$) and poly-4-vinylbiphenyl (PVB, $M_w = 450,000$) were prepared by anionic polymerization. A low molecular weight poly(ethylene oxide) (PEO) (Polyglycol E4000, Dow Chemical Co.), and a high molecular weight PEO (WSR-35, Union Carbide Chemicals Co.) were used as received. Polyblends were prepared by dissolving both polymers in benzene, followed either by precipitation with hexane, or by freeze drying. The resulting powder was then dried under vacuum at 40–50°C. Graft copolymers were prepared by polymerizing ethylene oxide onto poly-radical anions of PVN.^{1,2}

Young's modulus was determined with a torsional apparatus constructed according to ASTM standards (D 1053–61) using test specimens ($2 \times 1/4$ in. and 0.05–0.08 in. thick) prepared by compression molding at 55°C. and 1000–4000 psi.

The specific volume–temperature curves for the test specimens were obtained by using a mercury-filled capillary dilatometer. Specific volumes at 25°C., determined in a pycnometer, were used as reference.

X-ray diagrams were obtained on a General Electric XRD-3 diffractometer using copper $K\alpha$ radiation.

Results

The modulus curves of three blends of PEO E4000 (75, 50, and 25%) with PVN are shown in Figure 1 along with that for pure PVN. The 25% PEO blend shows a gradual decrease in modulus to about 100°C., follows a plateau to about 120°C., and then undergoes a transition similar to that of PVN.

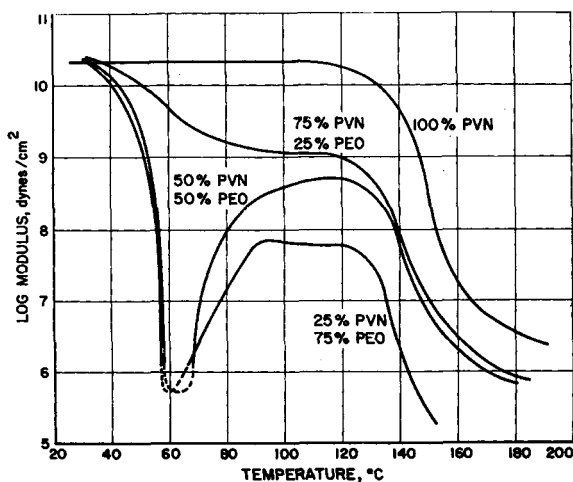


Fig. 1. Plots of log modulus vs. temperature for polymer blends of PVN and PEO.

An unusual behavior, however, was exhibited by the other two blends. At 58°C. the modulus dropped sharply, but with a further increase in temperature the modulus started to rise and went through a maximum at about 120°C. At the base of the "well," the modulus was too low to be measured. For comparison, Figure 2 shows the modulus curves for two blends of PEO E4000 (75 and 50%) with poly-4-vinylbiphenyl, and one blend of 50% PEO 4000 with polystyrene. None of these blends exhibited a well, and at high temperatures the samples became friable and broke. The difference in behavior between a blend and a graft copolymer of equal composition is illustrated in Figure 3.

The modulus curves for two 50/50 PVN blends (one with PEO E4000 and the other with WSR-35, the high molecular weight PEO), which are

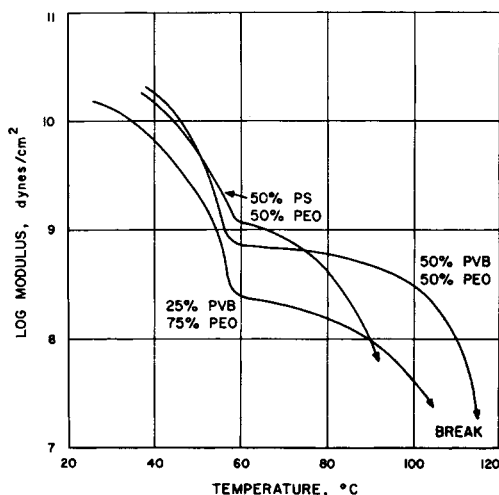


Fig. 2. Plots of log modulus vs. temperature for polymer blends of PVB and PS with PEO.

given in Figure 4 show that, except for a 20°C. shift in the position of the well, the increase in molecular weight of PEO did not modify the characteristic features of the curve. The "well" behavior for these blends was reversible as long as the temperature at which the peak occurred (ca. 120°C.) had not been exceeded, but once exceeded, the "well" behavior could not be reproduced, as illustrated by the two upper curves in Figure 4.

X-ray diagrams and dilatometric curves for three blends of PEO E4000 (75, 50, and 25%) with PVN are shown in Figures 5 and 6, respectively. For reference, curves for pure PEO E4000 are included. Both the 75 and 50% blends have x-ray diagrams characteristic of crystalline PEO and undergo a volume change at the PEO melting point, whereas the 25% blend exhibits completely amorphous behavior.

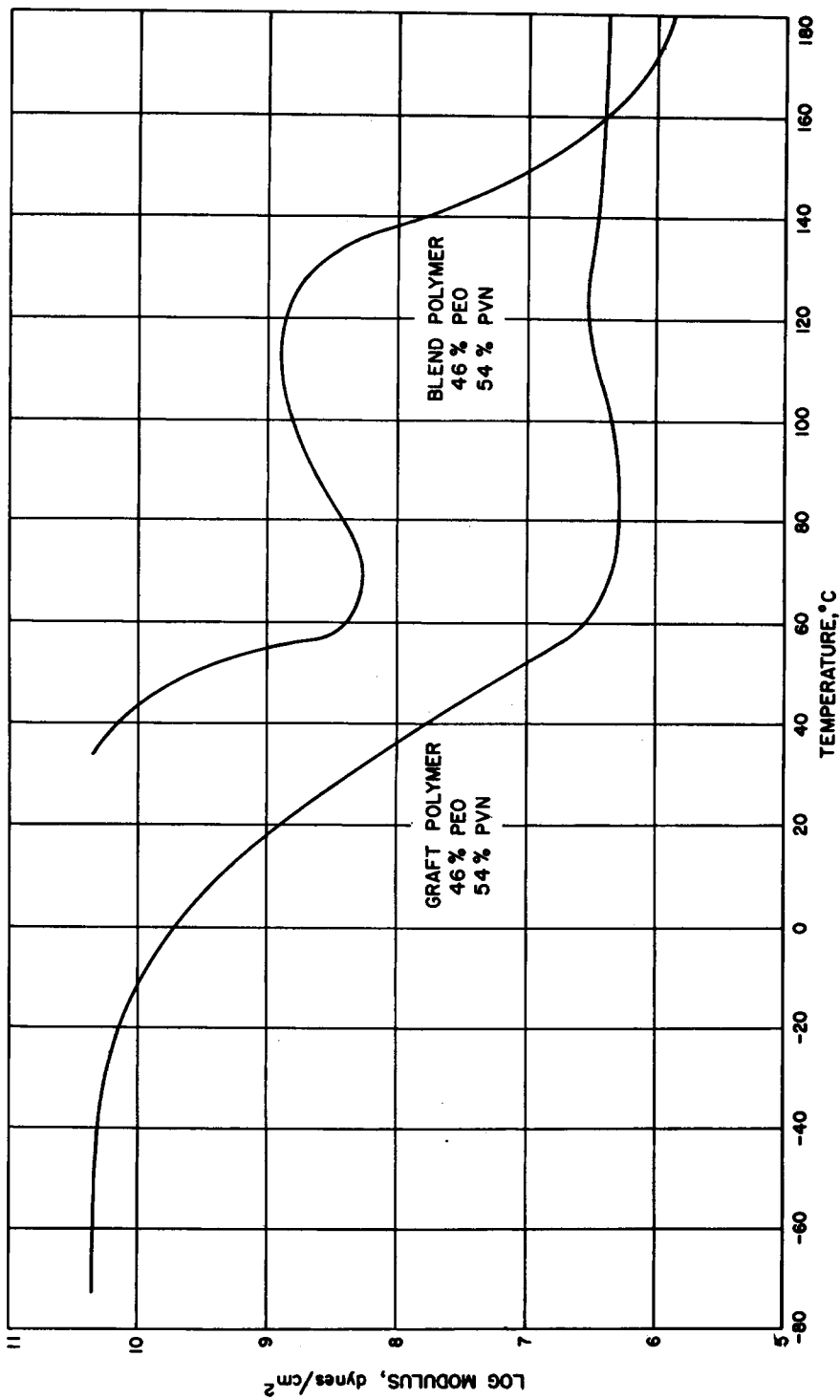


Fig. 3. Plots of log modulus vs. temperature for a blend and graft polymer.

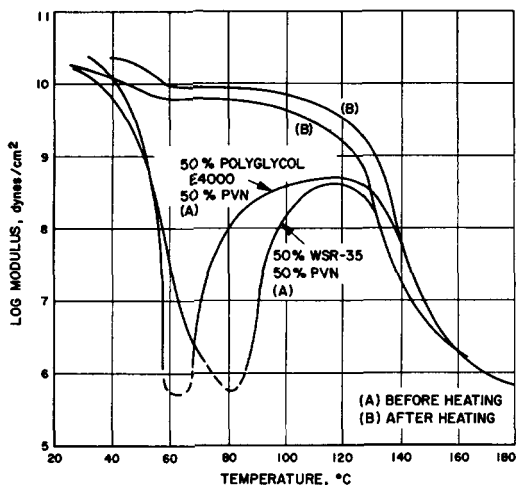


Fig. 4. Plots of log modulus vs. temperature for two 50/50 polymer blends of PVN with PEO of different molecular weights.

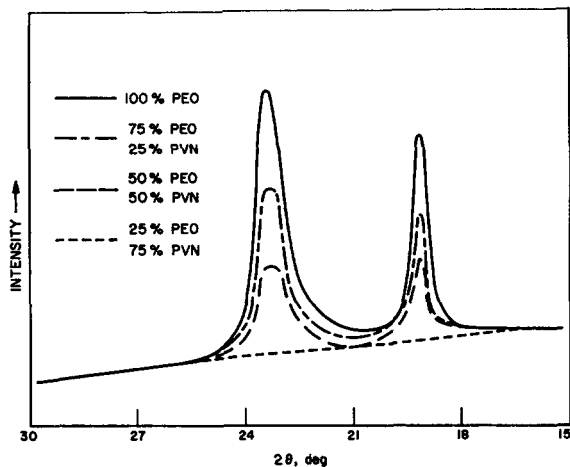


Fig. 5. X-ray diagram for polymer blends of PVN and PEO. (Measured at room temperature.)

Discussion

The discussion of the properties of the PVN-PEO preparations centers on two key experimental results. First, x-ray data at room temperature (Fig. 5) as well as volume changes at melting (Fig. 6) show qualitatively that although the 75 and 50% PEO blends exhibit crystallinity below the melting temperature, they contain significant amounts of amorphous PEO, and that the 25% blend is completely amorphous. Assuming additivity of volumes,³ calculations indicate that at 25°C. the crystalline part of both the 75 and 50% blends consists of PEO, whereas the amorphous part con-

tains 46% PEO and 54% PVN. The second important result is that the unusual phenomenon of a well in the modulus-temperature curves (Fig. 1) was observed only for the blends which exhibit crystallinity. The same rule was found to hold for graft copolymers. Based on these observations, the behavior of the blends could be interpreted by postulating that the amorphous PEO is bound to PVN to form a complex in the ratio of 3:1 monomer units (i.e., 46 wt.-% PEO to 54 wt.-% PVN), respectively.

The modulus curve for the blend having the composition of the "complex" (Fig. 3) exhibits a shallow well, showing indeed that changing the composition from 50% (Fig. 1) to 46% leads to a drastic change in behavior. The specimen may be described as leathery in this region. Above 60°C., droplets of liquid PEO began to appear on the surface of the test specimen, leaving behind a core of increasing PVN content which causes a slight rise

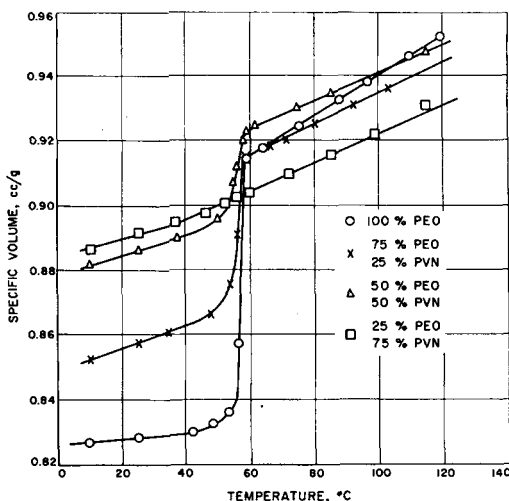


Fig. 6. Dilatometric curves for polymer blends of PVN and PEO.

in the modulus. Beyond 120°C., the specimen rapidly softens. The sweating out of the PEO is thought to be due to partial dissociation of the complex with increasing temperatures. This is consistent with an observation we made that PVN exhibits a negative temperature coefficient for its solubility in etherlike solvents. The dissociation of the complex is akin to the solvent-solute dissociations described by Doolittle.⁴

The large drop in modulus for the blends containing more than 46% PEO occurs when the crystalline PEO melts, and the specimens are then composed of liquid PEO and the softened leathery complex. With increasing temperatures, the modulus rises because, again, the complex dissociates and PVN forms colloidal particles which reinforce the system.

Modulus curves exhibiting wells have been previously reported for a blend of poly(vinyl chloride) and poly(vinylidene chloride)⁵ (PVLC), and for a sulfur-plasticized polysulfide rubber.⁶ The wells were obtained by

quickly cooling the melts to prevent crystallization of the PVLC and the sulfur. The rise in modulus is observed when the glass transition temperature for one of the components is exceeded, allowing the other (PVLC or sulfur) to crystallize. For these, the well could not be reproduced by gradually lowering the temperature. For the PVN-PEO system, x-ray measurements showed that this system is completely amorphous in the temperature region of increasing modulus and furthermore, the well for this system is reversible.

The fact that the "well" behavior could not be reproduced for samples heated beyond 120°C., suggested that PEO and PVN remain dissociated in separate phases, leading to the conclusion that the complex can be formed only if entanglement of the two polymers can be promoted. Therefore, it is reasonable to expect that the PEO-PVN complex had to be formed during the preparation of the blend in benzene, a good solvent for both polymers. In this solution, the two polymers are intimately entangled, which should lead to configurations favorable for the formation of the "complex." To test this hypothesis, dimethoxyethane, a poor solvent for both polymers, was used to prepare a blend under conditions unfavorable for intimate entanglement. This blend did not exhibit a well but instead gave a modulus curve resembling that of Figure 4B.

A different situation should exist for the graft copolymers in which one end of the PEO chain is attached to the PVN backbone. Three graft copolymers containing 20, 46, and 67% PEO were examined. The 20% PEO copolymer exhibited no well and showed no evidence of crystallinity by either x-rays or dilatometry. The 67% PEO copolymer exhibited a well, and the x-ray dilatometric results showed that it contained both crystalline and amorphous PEO. Once this copolymer was heated beyond 120°C., the well was not reproduced. An entirely different behavior was exhibited by the graft copolymer having the composition of the complex (46% PEO, Fig. 3). This material was transparent, rubbery, and had a glass transition temperature below -20°C. Furthermore, it retained its rubbery properties after being heated beyond 120°C. An additional interesting property is the existence of a plateau extending from about 60 to 180°C., characteristic of a crosslinked or very high molecular weight polymer.⁷ However, this material is readily soluble in most aromatic and ether-type solvents. This behavior may originate from entanglement of the PEO side chains of adjacent molecules.

None of the blends of polystyrene or poly-4-vinylbiphenyl contained significant amounts of amorphous PEO, indicating that the complex of PEO with these aromatic polymers could not be formed. The modulus curves for these systems are characteristic of blends of incompatible polymers. The same observations were made on graft copolymers of PVB and PEO. The incompatibility with PEO of these polymers and of PVN was demonstrated by their insolubility in melts of low molecular weight PEO. The reason for the apparently different behavior for these polymers as compared to PVN is not as yet understood, but there is strong evidence

from dilute solution studies that the conformational properties for these polymers differ markedly.

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Résumé

On a trouvé que le poly- β -vinylnaphtalène et l'oxyde de polyéthylène (54:46% en poids) forment des mélanges homogènes ou des copolymères greffés quand ils sont préparés dans des conditions qui inhibent la cristallisation de l'oxyde de polyéthylène. De telles préparations peuvent être obtenues à partir de solutions dans un bon solvant pour les deux composants par des procédés de précipitation qui conduisent à la formation de coacervats plutôt que de fractions, ou par lyophilisation. Les préparations contenant plus de 46% en poids d'oxyde de polyéthylène sont caractérisées par des courbes du module en fonction de la température possédant un minimum à environ 60°C. Ce comportement a été interprété comme étant dû à une séparation de la microphase ayant lieu avec une augmentation de température, procédé qui devient irréversible au-dessus de 120°C. Un copolymère greffé ayant la composition 54/46 était caoutchouteux à température de chambre et, contrairement aux mélanges ne présentait pas la transition vitreuse du poly- β -vinylnaphtalène à 138°C. La forte différence dans le comportement entre les polymères en mélange et les copolymères greffés est due au fait que dans le dernier cas la séparation irréversible de la microphase ne peut avoir lieu. Les propriétés décrites ci-dessus semblent être particulières au poly- β -vinylnaphtalène. De telles propriétés ne peuvent être reproduites dans les préparations de l'oxyde de polyéthylène avec le polystyrène, le poly-4-vinylbiphényle, ou le polyacénaphthylène. Ces préparations montrent un comportement caractéristique de mélanges de deux polymères incompatibles.

Zusammenfassung

Unter Bedingungen, welche die Kristallisation von Polyäthylenoxyd verhindern, bilden Poly- β -vinylnaphtalen und Polyäthylenoxyd (54:46 Gewichts%) homogene Mischungen oder Pfropfcopolymere. Solche Präparate können aus Lösungen in einem guten Lösungsmittel für beide Komponenten entweder durch Fällungsverfahren, welche zur Koacervierung und nicht zur Fraktionierung führen, oder durch Gefriertrocknung erhalten werden. Präparate mit mehr als 46 Gewichts% Polyäthylenoxyd wurden mit Modul-Temperaturkurven charakterisiert, die ein Maximum bei etwa 60°C zeigen. Dieses Verhalten wurde als eine mit zunehmender Temperatur eintretende Mikrophasentrennung interpretiert, ein Prozess, welcher oberhalb 120°C irreversibel wird. Ein Pfropfcopolymeres mit der 54:46-Zusammensetzung war bei Raumtemperatur kautschukartig und zeigte im Gegensatz zu den Polymermischungen nicht die Glasumwandlung bei 138°C von Poly- β -vinylnaphtalin. Der ausgeprägte Unterschied im Verhalten zwischen Polymermischungen und Pfropfcopolymeren ist durch den Umstand bedingt, dass bei letzteren eine irreversible Mikrophasentrennung nicht stattfinden kann. Die

oben beschriebenen Eigenschaften scheinen für das Poly- β -vinylnaphthalen spezifisch zu sein. Bei Präparaten aus Polyäthylenoxyd mit Polystyrol, Poly-4-binylbiphenyl oder Polyacenaphthalen konnten keine derartigen Eigenschaften reproduziert werden. Diese Präparate zeigten ein für Mischungen von zwei unverträglichen Polymeren charakteristischer Verhalten.

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