

# Colloidal and Morphological Behavior of Block and Graft Copolymers

# Colloidal and Morphological Behavior of Block and Graft Copolymers

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Edited by Gunther E. Molau

Polymer Science Group  
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## PREFACE

The molecules of block and graft copolymers are molecules of a higher order; they consist of homopolymer subchains which are interconnected by chemical valence bonds. This structural complexity is manifested in the unusual behavior of block and graft copolymers both in solution and in bulk. Many types of interactions are possible in block and graft copolymers in the solid state. Polymer subchains of one molecule can interact with other polymer subchains which may belong to the same molecule or to different molecules. Since polymer chains of chemically different composition are usually incompatible, thermodynamically unfavorable as well as thermodynamically favorable interactions exist in the solid state. In solutions of block and graft copolymers, the situation becomes even more complex, because interactions between the solvent molecules and the various subchains of the copolymer molecules occur in addition to the interactions between the polymer chains. This multitude of interactions gives rise to a wide spectrum of colloidal and morphological properties which have no parallel in less complex polymer systems such as homopolymers or random copolymers.

Research on the colloidal and morphological behavior of block and graft copolymers is a relatively new field of endeavor. It started in 1954, when F. M. Merrett fractionated mixtures of grafted natural rubber with the corresponding homopolymers and observed that colloidal sols were formed at certain points during his fractional precipitations. His further experiments with these sols showed that the same samples of grafted rubber could be obtained in the form of two different modifications, which he called "hard form" and "soft form." Merrett's colloidal sols and his hard and soft morphological modifications seem to be the first experiments reported in the literature which demonstrate that graft copolymers can have colloidal properties and that these properties can lead to the formation of different types of morphologies.

In the years following Merrett's discovery, further progress in this special area was slow. A few isolated papers appeared in

intervals of several years. Studies in France revealed that block copolymers of styrene and ethylene oxide can form liquid crystalline solutions. Work on high-impact polystyrenes and related systems in the United States showed that graft or block copolymers have an emulsifying effect in immiscible polymer solutions. In the last two to three years, the interest of the research community in the colloidal and morphological aspects of block copolymers has increased dramatically since the discovery was made that certain triblock copolymers of butadiene or isoprene with styrene are "thermoplastic rubbers" which act like crosslinked rubbers at room temperature but can be molded like regular thermoplastic materials at elevated temperatures. In addition to this discovery, the research interest was stimulated by the finding that butadiene or isoprene units in block copolymers or in rubber-modified polymer systems can be stained with osmium tetroxide, thus allowing direct observation of the stained portions of the polymer chains in the transmission electron microscope.

The Polymer Division of the American Chemical Society has sponsored a symposium which has focused, for the first time, on the colloidal and morphological aspects of research on block and graft copolymers. Under the title "Colloidal and Morphological Behavior of Block and Graft Copolymers," this symposium was held as a part of the 160th National Meeting of the American Chemical Society in Chicago, September 13-18, 1970. The purpose of the symposium was to present papers which are representative of the work currently being done on colloidal and morphological aspects of block and graft copolymers. At the same time, an attempt was made to bring people of different research areas together who could be expected to have mutual interests. These different but interrelated research areas are concerned with membranes, ionomers, urethane elastomers, and block and graft copolymers.

The symposium consisted of five half-day sessions. In the first session, the peculiar morphology of block copolymers was illustrated in papers on electron microscopy of block copolymers of styrene with butadiene or isoprene. A theoretical treatment followed which explained why the various types of morphological structures are formed. Block copolymers containing siloxane chains, which were newcomers in the field, were the subject of papers presented in the second session. The third session started with a special feature, a lecture on biological membranes. This lecture was given in order to make people interested in block copolymer morphology aware that biological membranes have structures which are, in many ways, analogues to structures observed with block copolymers. An interchange of ideas and knowledge between membrane technology and block copolymer morphology is desirable in the light of the current industrial interests in membranes, e.g., for desalination of water. Other papers in the third session

presented work on ionomers and on certain urethane elastomers, again materials which are analogous to block copolymers because they too have "physical crosslinks."

The fourth and fifth sessions covered papers on the emulsifying effect of block and graft copolymers, on colloidal aspects of high-impact polymers, and on the problem of microphase separation in block copolymers. One paper which presented work on the adsorption of block copolymer molecules on solid surfaces gives rise to the hope that better fractionation methods will be found based on the adsorption of block copolymers, e.g., in adsorption chromatography.

The symposium has covered a considerable portion of the work currently being carried out on colloidal and morphological behavior of block and graft copolymers and many researchers working in this field have participated. Previous published work in the same area is covered by a recent survey article also entitled "Colloidal and Morphological Behavior of Block and Graft Copolymers." This article has appeared as a part of another Plenum book which covers the proceedings of a recent symposium on general aspects of block copolymers (Proceedings of the Symposium on Block Polymers at the meeting of the American Chemical Society in New York City, September, 1969, published by Plenum Press, New York, 1970).

I would like to thank all authors for their fine cooperation in expediting the publication of this book and I am grateful to Dr. R. F. Boyer, Dr. J. K. Rieke, and Dr. D. R. Weyenberg for their presiding over three of the sessions.

September 26, 1970

Gunther E. Molau

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## MICROMORPHOLOGY-PROPERTY RELATIONSHIPS IN GRAFT AND BLOCK COPOLYMERS

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### INTRODUCTION

Graft and block copolymers composed of plastic and rubber components have attracted much attention because of their interesting combination of physical properties. ABS plastics which possess the rigidity of plastics and the toughness of rubbers at the same time are good examples. The properties of ABS have been realized by incorporating fine rubber particles in plastic matrix, i.e., by designing the phase structure. The importance of phase structure was first recognized when Kato<sup>(1)</sup> demonstrated microstructure of the ABS plastic clearly under the electron microscope by using his osmium tetroxide ( $\text{OsO}_4$ ) staining and hardening procedure. With the aid of Kato's method, it has now become possible to study the micromorphologies in plastic-rubber systems and to correlate them with their physical properties. This method of investigation has been quite new in this field and supplements the traditional method of setting up a hypothesis, carrying out the experiments and modifying the hypothesis.

An accumulation of the data on the morphology-property relationship may lead us to a new field, POLYMEROGRAPHY,<sup>(2,3)</sup> proposed after the name of Metallography. In POLYMEROGRAPHY, attempts are being made to systematize the phase structure - property relationships mainly by the use of electron microscopy. Moreover, it is intended to develop a new property by creating

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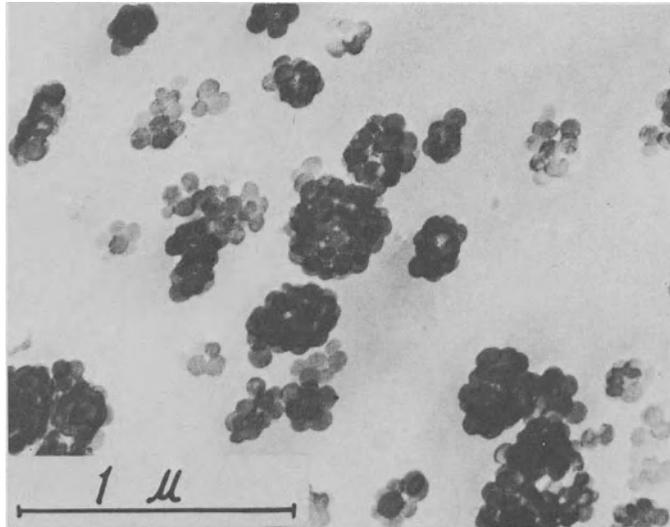
a new phase-structure based on the above systematization. This type of investigation in polymers, however, has had only a short history and unfortunately many results are often kept secret by those hoping to exploit the commercial development. In the present paper, several examples of POLYMEROGRAPHY which, we believe, are still in germination step will be discussed.

#### ABS POLYMERS AS AN IMPACT MODIFIER OF PVC

In order to improve the impact properties of rigid PVC without sacrificing its transparency, specially prepared ABS (or MBS) graft copolymers are mixed with PVC. To retain the transparency, it is basically required to match the refractive index of the modifier with that of PVC and at the same time, to reduce its particle size to less than ca.  $0.1\mu$  in diameter. However, such a reduction of particle size usually causes a decrease of impact strength. Consequently, many research works have concentrated on the grafting technique to improve the impact strength. As a result, one of the interesting patents described that the addition of a large amount of water soluble salt in the grafting process resulted in an improvement of impact strength.<sup>(4)</sup>

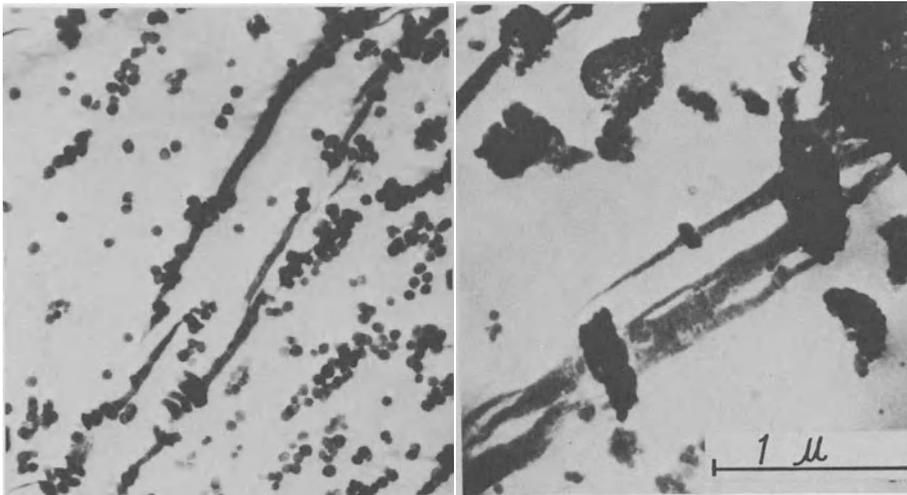
The ABS modifiers for the present study have been prepared by carrying out the emulsion polymerization of acrylonitrile (AN) and styrene (ST) monomers in the presence of polybutadiene rubber latex, with or without addition of salt according to the above patent. When 10 parts of modifier, prepared in the presence of salt, are blended with 100 parts of PVC, the Charpy impact strength of  $15 \text{ Kg.cm/cm}^2$  was obtained. This is much higher than the case where no salt was added,  $8 \text{ Kg.cm/cm}^2$ . Transparency of the former did not decrease to a noticeable degree. The electron micrograph of an ultrathin section of the ABS-modified PVC (with the addition of salt) is shown in Fig. 1. It is interesting to note that the modifier particles form a cluster of  $0.1$  to  $0.3\mu$  in diameter, and that a part of the grafted AN-ST copolymer seems to be included in the cluster. On the contrary the ABS modifier without salt exhibited a single particle dispersion in the PVC matrix. It is thus reasonable to consider that the cluster itself behaves as a large particle against the external stress thus causing a high impact strength, whereas optically it behaves as if it were divided into the original individual particles.

Another interesting property of this polymer system is that only a faint stress-whitening is observable when a properly prepared sample is subjected to bending or tensile stress under a relatively low strain rate. This is unusual for a rubber-modified plastic. Figure 2 shows the electron micrographs of



Ultrathin section of ABS-modified PVC prepared by adding salt at the grafting process.

Fig. 1



Crazing behavior of ABS-modified PVC.  
Left: faint whitening; right: extensive whitening.

Fig. 2

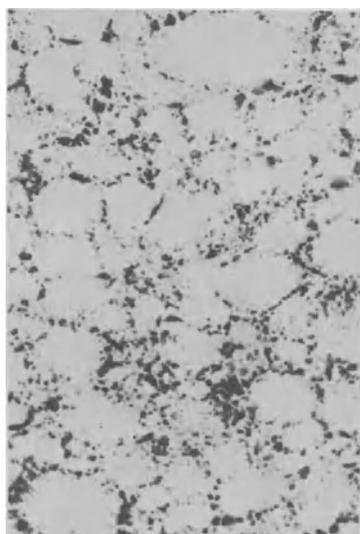
the portion of the specimen under stress for the two extreme samples: one with a faint whitening (left) and the other with an extensive whitening (right). It is clear from these pictures that the former exhibits a single particle dispersion (ca. 700 Å in diameter) and the stress-crazes,<sup>(5,6,7)</sup> which were found to be the cause of whitening, are as thin as the diameter of the single particle. On the other hand, the craze thickness of the latter is fairly wide, reflecting the clustering of individual particles to a great extent. It is, therefore, concluded that in the ABS-modified PVC crazes develop in the same way as the straight ABS does,<sup>(7)</sup> and that when the craze thickness is small enough one can hardly detect the whitening from the appearance.

### PVC-EVA GRAFT COPOLYMERS

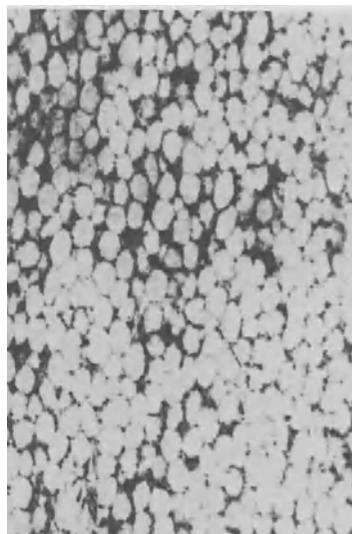
The commercially available graft copolymers such as ABS polymers generally include unsaturated rubbers. The attempts to utilize saturated rubbers for obtaining a better weatherability have been conducted in many places. One of the interesting systems is a graft copolymer composed of PVC and ethylene-vinylacetate rubber (EVA):

PVC/EVA graft copolymers for the present study have been prepared by dissolving the EVA rubber in VCl monomer, followed by a usual suspension polymerization of the monomer. Four samples of the composition, PVC/EVA = 95/5, 80/20, 70/30 and 50/50 were prepared. For the observation of micromorphology an additional step has been introduced before the application of the Kato's method: treatment of a sample with a saturated solution of NaOH in methanol at its refluxing temperature for one hour. By this treatment the EVA phase near the sample surface becomes susceptible to the staining with OsO<sub>4</sub>.

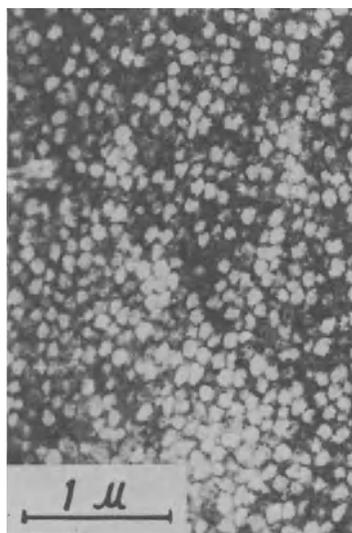
In the sample containing 5% EVA the impact strength is improved by a factor of 10 as compared with rigid PVC. Surprisingly however, the flow property is also improved to a considerable extent. When the EVA content is further increased a variety of properties, from a semirigid PVC to a soft PVC which has comparable mechanical properties to a plasticized PVC, can be obtained. Figure 3 shows the electron micrographs of PVC/EVA graft copolymers with varying EVA content. The sample containing 5% EVA shows that the EVA phase forms a network which separates the PVC matrix into particles with ca. 0.5μ in diameter. With the increase of EVA content, the mesh of the network decreases and the thread becomes thicker. The structure of the sample containing 50% EVA can be described as the EVA matrix containing dispersed PVC particles. It is likely that both components are contaminated with each other to some extent.



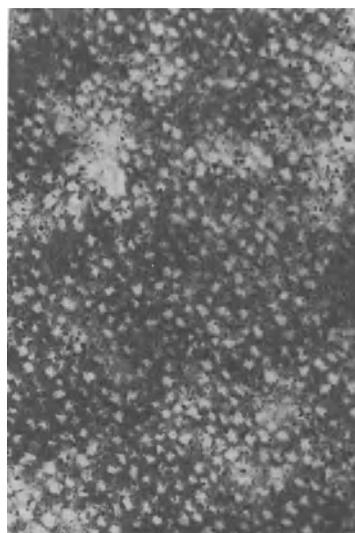
95/5



80/20



70/30



50/50

Ultrathin sections of PVC/EVA graft copolymers

Fig. 3

From these micrographs one can get some information on the properties described above. At first, it is reasonable to consider that the network formation of the rubber phase in a plastic matrix may serve to prevent an interfacial separation. Moreover, it favors the craze initiation and propagation without forming serious cracks as already discussed in a previous paper.<sup>(7)</sup> This may be a good reason for high impact strength. Secondly, the excellent flow property can be understood, if it is assumed that PVC phases separated by the thin EVA network flow as one flow unit.<sup>(8)</sup> In other words, it is likely that the EVA phase, which may be contaminated partially with PVC, serves as a lubricant at high temperature and binds the PVC phases together when the sample is cooled down to room temperature. On the other hand, the morphologies of PVC/EVA system with much higher EVA content seem to resemble EVA rubber filled with PVC particles. In this case, again both components are considered to be contaminated with each other. It has been reported that this type of structure, i.e., the elastomer filled with plastic particles, is found in styrene-butadiene block copolymers, where the plastic particles contribute to the reinforcement of the elastomer matrix.<sup>(9)</sup> It is thus easy to understand the excellent properties of this material as a soft PVC.

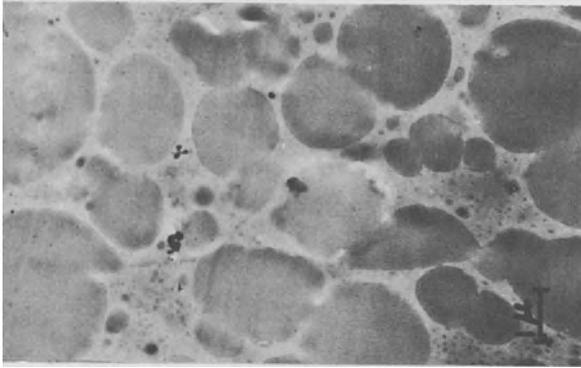
#### POLY(URETHANE-UREA)/POLYACRYLATE INTERPENETRATING POLYMER NETWORKS<sup>(10)</sup>

Interpenetrating polymer networks (IPN) have been prepared by carrying out a polymerization or crosslinking operation of one component in the presence of the other component polymer.<sup>(11,12)</sup> Although they are slightly different from graft copolymers, they are similar to them in the sense that the phase structure governs the properties. In the present study, poly(urethane-urea) latex provided by Wyandotte Chemical Corp. and self-curable polyacrylate latex supplied by B. F. Goodrich Chemical Co. were used as the starting materials. They are mixed together homogeneously and dried, followed by heating at 120°C to induce a crosslinking in both components. Dynamic mechanical measurements showed two distinct transition regions, at -20°C and 30°C, each corresponding to the glass transition temperature (T<sub>g</sub>) of component homopolymer.

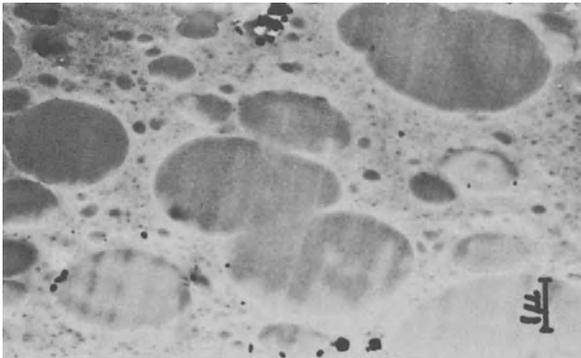
Figure 4 shows typical electron micrographs of ultrathin sections for three IPN's, A/U = 70/30, 50/50 and 30/70, where A and U designate polyacrylate and poly(urethane-urea) components, respectively. The dark phase represents the poly(urethane-urea) phase selectively stained by OsO<sub>4</sub>. It is clear that for A/U = 70/30 and 50/50 the poly(urethane-urea) particles of 1 to 5μ in diameter are dispersed in the polyacrylate matrix. At the composition A/U = 30/70, however, the poly(urethane-urea) particles seem to be in contact with each other to form a continuous phase. In other words, phase inversion occurs from "U particles in A matrix" to "A particles in U matrix" at the composition A/U = 30/70 as the U component increases. It is interesting to note that this



30/70



50/50



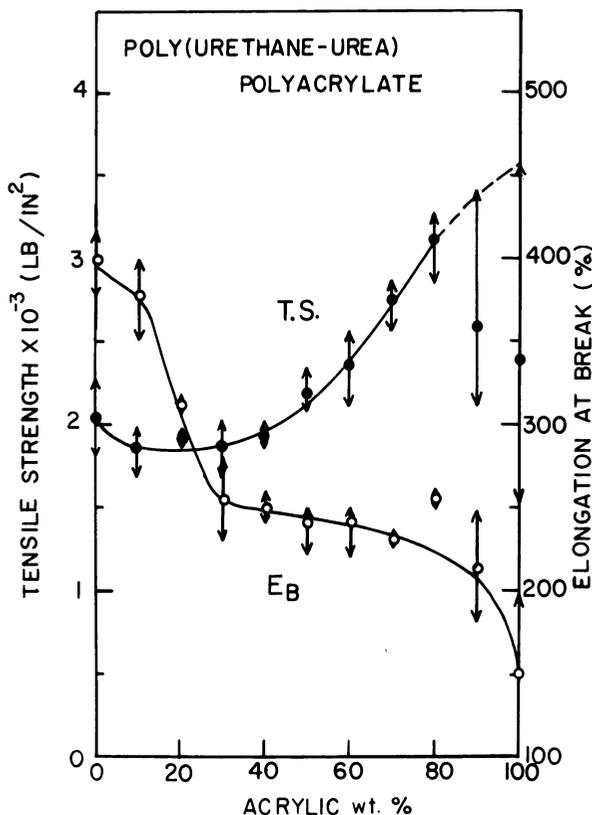
A/U = 70/30

Ultrathin section of poly(urethane-urea)/polyacrylate interpenetrating polymer networks.

Fig. 4

composition corresponds to that of the closest packing of particles.

Tensile measurements were carried out with the strain rate of  $5 \text{ min.}^{-1}$ . Results are shown in Fig. 5. Tensile strength does not increase until the polyacrylate (rigid) phase becomes continuous at  $A/U = 40/60$ . It increases thereafter almost linearly as the rigid phase increases. The elongation at break decreases rather rapidly until the rigid phase becomes continuous (at  $A/U = 40/60$ ) and then remains almost constant. It is thus concluded that the tensile properties are considerably governed by the phase structure formation.



Effects of tensile strength and elongation at break of poly(urethane-urea)/polyacrylate system measured at the strain rate of  $5 \text{ min.}^{-1}$  on polyacrylate content (rigid phase)

Fig. 5