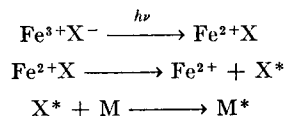


munication we wish to report two new methods of grafting methyl methacrylate to natural rubber in latex form.

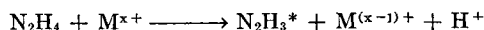
One procedure consists in irradiating commercial natural rubber latex in the presence of a vinyl monomer with ultraviolet light using water-soluble photosensitizers, such as ferric ion pairs $\text{Fe}^{3+}\text{Cl}^-$ and $\text{Fe}^{3+}\text{OH}^-$, in a nitrogen atmosphere. The mechanism of such photopolymerizations has been the subject of a detailed investigation,^{2,3} and it has been shown that the primary photochemical process involves an electron transfer followed by the dissociation of the primary product to generate a free radical which initiates vinyl polymerization:



where X represents a radical, e.g., Cl or OH, and M is the vinyl monomer.

In a typical experiment, when 200 cc. of rubber latex containing approximately 5 g. of total solids/100 cc. were irradiated with 2.8 g. of methyl methacrylate monomer using the $\text{Fe}^{3+}\text{Cl}^-$ photosensitizer, nearly 75% of methyl methacrylate was grafted to natural rubber. It is of interest to report that in similar experiments with acrylonitrile, no grafting was achieved although there was considerable homo-polymer, formation.

Another procedure consists in the use of hydrazine as the initiator of polymerization in emulsion. The mechanism of initiation of polymerization by hydrazine has been investigated in this laboratory,⁴ and evidence has been obtained in favor of an initiation reaction involving the hydrazyl radical formed by one-electron oxidation of hydrazine by metallic ion under the appropriate reaction conditions.⁵



where M^{*+} represents a one electron oxidant.

In the presence of oxygen, the primary process must presumably be the same since a direct reaction between hydrazine and oxygen is considered improbable.⁶ When methyl methacrylate is polymerized in the presence of commercial natural rubber latex using hydrazine under conditions of autoxidation of the latter catalyzed by cupric ions, a considerable amount of grafting was achieved. In a typical experiment where 28 g. of methyl methacrylate was polymerized in commercial latex containing about 40 g. of total solids under conditions of autoxidation of hydrazine with 10^{-4}M cupric ions as the catalyst at room temperature, the reaction was complete in six hours with nearly 50% of the methyl methacrylate grafted to the rubber. The graft copolymer, pure rubber, and polymethyl methacrylate were separated by using the appropriate solvent extraction procedures which have been employed by previous investigators.⁷

The details of this investigation, together with the properties of the graft copolymers prepared from rubber and various vinyl monomers, will be the basis of a subsequent publication.

References

1. L. C. Bateman, *Ind. Eng. Chem.*, **49**, 704 (1957).
2. M. G. Evans, M. Santappa, and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

3. C. C. Menon and M. Santappa, *Can. J. Chem.*, **35**, 1267 (1957).
4. C. C. Menon and S. L. Kapur, *Current Sci. (India)*, **27**, 245 (1958).
5. C. C. Menon and S. L. Kapur, unpublished results.
6. W. C. E. Higginson, *Chem. Soc. (London)*, *Spec. Publ. No. 10*, 105 (1957).
7. B. C. Sekhar, *Rubber Chem. & Tech.*, **31**, 430 (1958).

C. C. MENON
S. L. KAPUR

Division of Polymer Chemistry
National Chemical Laboratory
Poona-8, India

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Thermodynamic Parameters of Poly(ethylene Oxide) in Aqueous Solution

Recently, the results of an extensive study of the solution properties of high molecular weight poly(ethylene oxide) were discussed by the authors.¹ One of the major points of interest in this study was the inverse solubility-temperature relationship of this polymer in water solution. This phenomenon was interpreted in terms of a hydrophilic-hydrophobic balance in the polymer structure and in terms of the

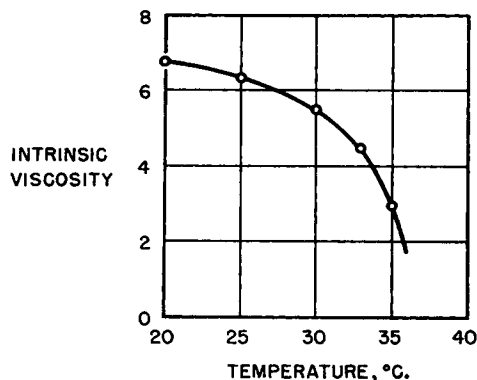


Fig. 1. Intrinsic viscosity of a high molecular weight poly(ethylene oxide) at temperatures near the upper limit of solubility in 0.45 M potassium sulfate solution.

increase in the activity of the neutral polymer molecule as the temperature was increased. A further insight into the factors determining the solution properties of this polymer can be gained following the theory of Fox and Flory² with respect to the temperature dependence of the intrinsic viscosity.

In Fig. 1, the intrinsic viscosity of a sample of poly(ethylene oxide), of about four million molecular weight, is shown as a function of temperature in 0.45 M potassium sulfate solution. If 35°C. is taken as the precipitation temperature of an infinite molecular weight polymer, then using the expression for the molecular expansion factor, α , of Fox and Flory²

$$\alpha^5 - \alpha^3 = 2C_M\psi_1[1 - (\theta/T)]M^{1/2}$$

the thermodynamic parameters of poly(ethylene oxide) in this solution can be estimated. This is done in Figures 2 and 3 where the data for the temperature dependence of the intrinsic viscosity of polyisobutylene in benzene² are compared with that of poly(ethylene oxide) in potassium sulfate solution. An appropriate correction for the temperature dependence of the parameter, C_M , is applied by multiplying by the ratio of the constants K_T and K_θ , the constants of the intrinsic viscosity-molecular weight equation at the respective temperatures.

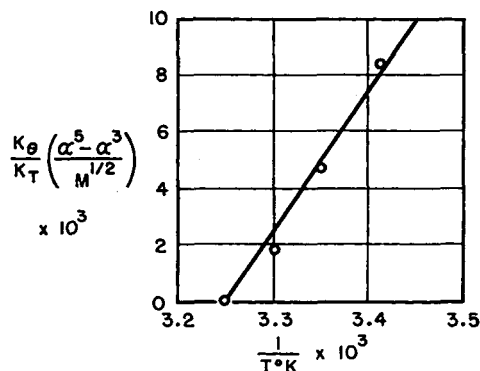


Fig. 2. Poly(ethylene oxide) in 0.45 M K_2SO_4 .

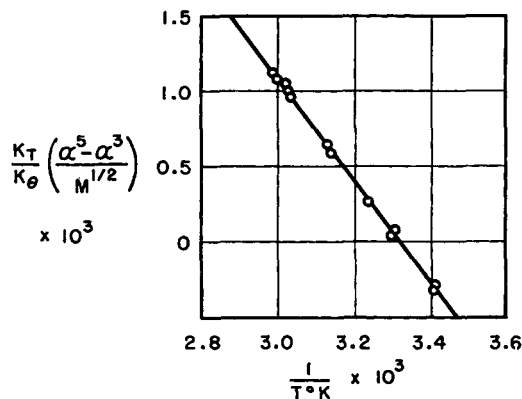


Fig. 3. Polyisobutylene in benzene.²

It is noted that the curves of Figures 2 and 3 have opposite slopes. The negative slope of the curve for polyisobutylene in benzene is the expected result for a polymer in a poor solvent in which both the heat of dilution and entropy of dilution are positive. The opposite slope of the curve for poly(ethylene oxide) in potassium sulfate solution is interpreted as the result of the heat of dilution and entropy of dilution in this case being negative. (The entropy and heat of dilution parameters can be calculated from the slope of the curve, Figure 2, since $2C_M\psi_1\theta = -49$ and $\theta = 208^\circ K$.)

The negative entropy of dilution and heat of dilution of poly(ethylene oxide) in aqueous solution implies a high degree of polymer-solvent interaction and doubtless the orientation of solvent with respect to the polymer chain. The existence of a lower consolute temperature in water solutions of higher poly(ethylene glycols) and the extensive measure-

ments of Malcolm and Rowlinson³ tend to confirm the view that negative entropies of dilution control the solution properties of poly(ethylene oxide) resins in water. The unusual pseudo-plastic character of fairly concentrated solutions of the higher molecular weight polymers in water⁴ may also be a result of the "entropy control" of the flow of these solutions.

References

1. F. E. Bailey, Jr., and R. W. Callard, *J. Appl. Polymer Sci.*, **1**, 56 (1959).
2. T. G. Fox, Jr., and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1909 (1951).
3. G. M. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).
4. F. E. Bailey, Jr., G. M. Powell, and K. L. Smith, *Ind. Eng. Chem.*, **50**, 6 (1958).

F. E. BAILEY, JR.
R. W. CALLARD

Research Department
Union Carbide Chemicals Company
South Charleston, West Virginia

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Effect of Carbon Black on TMTD Vulcanization*

It has been shown previously that it is possible to obtain an estimate of the amount of tetramethylthiuram disulfide (TMTD) required to produce one crosslink, and of the amount of firmly bound sulfur formed per crosslink, during the vulcanization of natural rubber by comparing stress-strain properties of gum rubber samples vulcanized with TMTD and with cumyl peroxide.¹ The earlier work led to values of 3.8 molecules of TMTD and 1.9 atoms of sulfur per crosslink in the presence of sufficient zinc oxide to obtain maximal crosslinking. By direct application of the absolute calibration of crosslink density by Moore and Watson,² Moore has subsequently arrived at values of 3.6 and 3.0, respectively, for these quantities.³ Partly on theoretical grounds, Bevilacqua⁴ has since concluded that in the reactions leading to crosslinking the expected values should be three of TMTD and two of sulfur. These values would also be expected on the basis of the mechanism discussed by Bielstein and Scheele.⁵

It is widely believed that there is chemical interaction of carbon black with rubber during vulcanization as well as during processing.⁶ The nature of this interaction has not been elucidated. If hydrocarbon radicals interact with black and the same radical intermediates are formed in TMTD vulcanization and in peroxide vulcanization, the effect of carbon black should be the same with each vulcanizing system. Alternatively, if there is no or negligible interaction between the black and the rubber during vulcanization, the superficial effect of carbon black should be identical in the two systems. In either event it should be possible to make the same sort of comparison which was previously re-

* This is contribution number 182 from these laboratories.