this general equation. The theory of irreversible polarographic waves previously developed[6,7] is applicable when the rate constant at the standard potential is smaller than approximately 5×10^{-5} cm. sec.$^{-1}$. Experimental quasi-reversible waves which correspond to values of k_s from 5×10^{-5} to 2×10^{-2} cm. sec.$^{-1}$ can still be interpreted although the method is somewhat awkward. Processes for which k_s is larger than 2×10^{-2} cm. sec.$^{-1}$ yield reversible waves, and no information on the kinetics of these electrode processes can be obtained from polarographic data. Other methods such as electrolysis with superposed alternating voltage have to be used.[24] The latter method can be applied[25] for values of k_s up to 1 cm. sec.$^{-1}$, but markedly irreversible processes cannot be studied by this method. Thus, the polarographic method and electrolysis with superposed alternating voltage are the complement of each other in the study of the kinetics of electrode processes.

Note on a Review by Tanford and Wawzonek (Added after the completion of this manuscript)

There appeared recently a review[26] of polarography in which it is stated that we claimed "entirely without foundation" that our treatment of irreversible waves is more general than previous theories.[4,5] Since an authoritative character is conferred to this statement by its publication in a well-known series on physical chemistry, the author feels compelled to challenge this remark.

Tanford and Wawzonek failed to recognize one fundamental point, namely, that *the mass transfer problem is solved rigorously in our treatment* (at least for the linear case), whereas the *Nernst diffusion layer theory is applied in the previous papers on this question.* It is generally possible to apply the Nernst diffusion layer theory to any problem of mass transfer, but results derived in this manner are approximate since the concept of diffusion layer is somewhat artificial.[27] In the case of irreversible waves, for example, the diffusion layer thickness is an unknown function of the rate of the electrode process, and this unknown function is contained implicitly under the form of the diffusion layer thickness in the equations for the irreversible waves derived by previous investigators.

This remark is not made to deny any value to previous work on irreversible waves, but merely to point out the significance of our contribution.

Acknowledgment.—This investigation is part of the project NR-051-258 which is sponsored by the Office of Naval Research. The author gladly acknowledges the support of this organization. Mr. Berzins carried out the numerical calculations involved in the construction of Fig. 1.

[24] J. E. B. Randles, *Discussion Faraday Soc.*, **1**, 11 (1947); B. Ershler, *ibid.*, **1**, 269 (1947), *J. Phys. Chem., U.S.S.R.*, **22**, 683 (1948); H. Gerischer and K. Vetter, *Z. physik. Chem.*, **197**, 92 (1951); D. C. Grahame, "Mathematical Theory of the Faradaic Admittance," Technical Report to the Office of Naval Research, No. 8 (1952).

[25] J. E. B. Randles, *Trans. Faraday Soc.*, **48**, 828 (1952).

[26] Article by C. Tanford and S. Wawzonek in "Annual Review of Physical Chemistry," G. K. Rollefson and R. E. Powell, Editors, Annual Reviews, Stanford, Calif., 1952. See p. 255.

[27] L. L. Bircumshaw and A. C. Riddiford, *Quart. Rev. Chem. Soc.*, **6**, 157 (1952).

BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM THE PLASTICS RESEARCH LABORATORY OF THE MONSANTO CHEMICAL COMPANY]

Effects of Chemical Heterogeneity in Copolymers on Some Physical Properties

BY LAWRENCE E. NIELSEN

RECEIVED SEPTEMBER 3, 1952

Homogeneous copolymers in which all the molecules have the same chemical structure and heterogeneous copolymers in which the chemical composition varies from molecule to molecule have been prepared. Several such vinyl type copolymer systems were investigated. Proof of chemical hetereogeneity was obtained by fractionations and chemical analysis. The dynamic shear modulus and mechanical damping were measured over a temperature range. The damping goes through a maximum at the transition temperature while the modulus changes greatly in the transition region. The heterogeneous copolymers have a much broader transition (softening) region than the homogeneous ones. Mixtures of two polymers were investigated. Dynamic mechanical tests are sensitive to changes in chemical heterogeneity, molecular aggregation, and freedom of molecular motion in high polymeric materials.

Introduction

The literature contains many references[1] on the preparation of copolymers and on the determination of monomer reactivity ratios. However, very little has been published on the chemical heterogeneity of copolymers and its effects on various physical properties. Skeist[2] has developed a method of computing the chemical heterogeneity of a copolymer, and deButts[3] has given a method of integrating the rate equations while Wall[4] has shown experimentally that chemical heterogeneity can exist in rubber-like copolymers.

In general the chemical composition of copolymer molecules is not uniform but varies during the course of the polymerization reaction. The first molecules formed are rich in the more reactive component while the molecules formed at the end of the reaction are rich in the less reactive component. Thus, there results a heterogeneity in the chemical composition of the copolymer. In many respects it is expected that changes in physical properties are more dependent upon the degree of heterogeneity than upon such factors as variations in molecular weight where each polymer segment is the same and finds itself in essentially the same type of neighborhood or force fields as every other segment.

Several copolymers have been prepared which

[1] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[2] I. Skeist, THIS JOURNAL, **68**, 1781 (1946).

[3] E. H. deButts, *ibid.*, **72**, 411 (1950).

[4] F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, *ibid.*, **70**, 1031 (1948).

vary in degree of chemical heterogeneity from very homogeneous materials to very heterogeneous ones. Mixtures of two polymers, which are cases of extreme heterogeneity, have also been studied. In some cases the heterogeneity of materials has been proved by fractionation and subsequent chemical analysis of the fractions.

A new physical tool has been used for studying chemical heterogeneity, molecular compatibility (solubility) and variations in molecular environment for high polymers. This tool is dynamic mechanical tests made over a temperature range. In such tests the response of the high polymeric material to an alternating force is measured. An elastic modulus and a damping or energy dissipation term are calculated from the results. Similar tests have been used in the field of chemical metallurgy with considerable success.[5]

Experimental

Table I lists some of the materials investigated along with their over-all chemical composition, degree of chemical heterogeneity, and intrinsic viscosity in methyl ethyl ketone. The styrene–methyl acrylate copolymers were prepared by mass polymerization in large sealed test-tubes using benzoyl peroxide as catalyst. Polymerization was started at 60° and the temperature gradually increased during the course of the polymerization. The homogeneous material was prepared by stopping the reaction at about 7% conversion and purification of the polymer by thrice repeated solution in benzene followed by slow precipitation in methanol. The material was then dried at 70°. The corresponding heterogeneous copolymer was prepared by allowing the polymerization to go to completion. This material was purified by dissolving in benzene and reprecipitating with methanol.

TABLE I

Copolymer	Composition	[η]	Heterogeneity
Styrene–methyl acrylate	55% styrene	2.82	Very homog.
Styrene–methyl acrylate	55% styrene	2.40	Heterogeneous
Vinyl chloride–methyl acrylate	59% V. C.	2.49	Homogeneous
Vinyl chloride–methyl acrylate	59% V. C.	2.37	Very heterog.
Vinyl chloride–β-cyanoethoxyethyl acrylate	50% V. C.	Insoluble	Homogeneous
Vinyl chloride-β-cyanoethoxyethyl acrylate	49% V. C.	Insoluble	Very heterog.

The vinyl chloride copolymers were made by emulsion polymerization using a persulfate oxidation–reduction catalyst at 40°. The heterogeneous copolymers were made by mixing the monomers in the proper proportion and carrying the reaction to completion. The homogeneous copolymers were made by keeping the concentration ratio of monomers constant during the course of the reaction by adding from time to time small quantities of the more reactive monomer similar to the method described by Fikentscher and Hengstenberg.[6] Considerable difficulty was experienced in keeping the monomer concentration ratio exactly constant, so the homogeneous copolymers are actually somewhat heterogeneous.

The mixture of polyvinyl chloride and butadiene–acrylonitrile copolymer is a commercially available material made by the B. F. Goodrich Company under the name of Geon Polyblend 500×479. It contains 70% polyvinyl chloride. The components of this mixture are soluble in one another as indicated by the transparency of films made from it. The polystyrene mixture with an added styrene–butadiene rubber is a typically insoluble mixture of polymers as indicated by the cloudy appearance of films made from it. Data on similar mixtures have been published.[7]

In order to verify experimentally that chemical heterogeneity existed in some of the materials, fractionations were carried out. To emphasize chemical structure differences rather than differences in molecular weight, a cross-fractionation technique was used for the vinyl chloride copolymers. The copolymers were dissolved in benzene and fractionated into two portions by adding enough methanol to slowly precipitate roughly half of the material. Each of these portions was later dissolved in methyl ethyl ketone and again partially precipitated with methanol. The vinyl chloride fractions were analyzed for chlorine by the Parr bomb technique and also by means of their infrared spectra. The chlorine analyses are listed in Table II. The heterogeneous styrene–methyl acrylate fractions were analyzed by taking the ratio of the optical density of two infrared absorption bands at 14.25 and 7.98 μ. The results in Table II clearly indicate a chemical heterogeneity. A manifestation of chemical heterogeneity was also observed in the solution viscosity of the styrene copolymer fractions. The fractions giving the most viscous solutions in benzene gave the least viscous solutions when dissolved in methyl ethyl ketone.

TABLE II

ANALYSES OF COPOLYMER FRACTIONS

Copolymer	Fraction	Chlorine, %	Ratio of optical densities
Homog. vinyl chloride–methyl acrylate	1	33.9	
	2	35.6	
	3	30[a]	
	4	29.8	
Heterog. vinyl chloride–methyl acrylate	1	38.0	
	2	34.4	
	3	32.7	
	4	20.9	
Heterog. styrene–methyl acrylate	1		1.74
	2		1.60
	3		1.49
	4		1.46

[a] From infrared determination.

The dynamic mechanical tests were made by a recording torsion pendulum, which has been described previously.[8] With this instrument a strip of the test material is attached to a freely vibrating moment of inertia disk so that the strip is alternately twisted and untwisted. An electrical transducer converts the mechanical motion into an electrical potential which is recorded on a chart. From the dimensions of the specimen, the moment of inertia of the system, and the period of the oscillations, it is possible to calculate the elastic shear modulus. The damping (logarithmic decrement) is calculated from the rate of dying out of the oscillations. The frequency of the oscillations was not kept constant but was usually in the range of 1/4 to 1 cycle/second. Tests were carried out in a large temperature chamber which could be varied from −50 to 150°.

Results and Discussion

The dynamic mechanical data on the styrene–methyl acrylate copolymers are shown in Fig. 1. It is generally characteristic of non-crystalline thermoplastic polymers to behave in the illustrated manner.[9]

At temperatures below the second-order transition temperature the modulus is high and the damping relatively small. In the transition or softening range the modulus decreases very rapidly while the damping becomes very large and goes

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(5) C. Zener, "Elasticity and Anelasticity in Metals," Univ. of Chicago Press, Chicago, Ill., 1948; R. Cabarat, L. Guillet and R. LeRoux, *J. Inst. Metals*, **75**, 391 (1949); A. S. Nowick, *J. Appl. Phys.*, **22**, 925 (1951).

(6) H. Finkentscher and J. Hengstenberg, U. S. Patent 2,100,900 (1937).

(7) R. Buchdahl and L. E. Nielsen, *J. Appl. Phys.*, **21**, 482 (1950).

(8) L. E. Nielsen, *Rev. Sci. Instruments*, **22**, 690 (1951).

(9) A. W. Nolle, *J. Polymer Sci.*, **5**, 1 (1950); L. E. Nielsen, R. Buchdahl and R. Levreault, *J. Appl. Phys.*, **21**, 607 (1950).

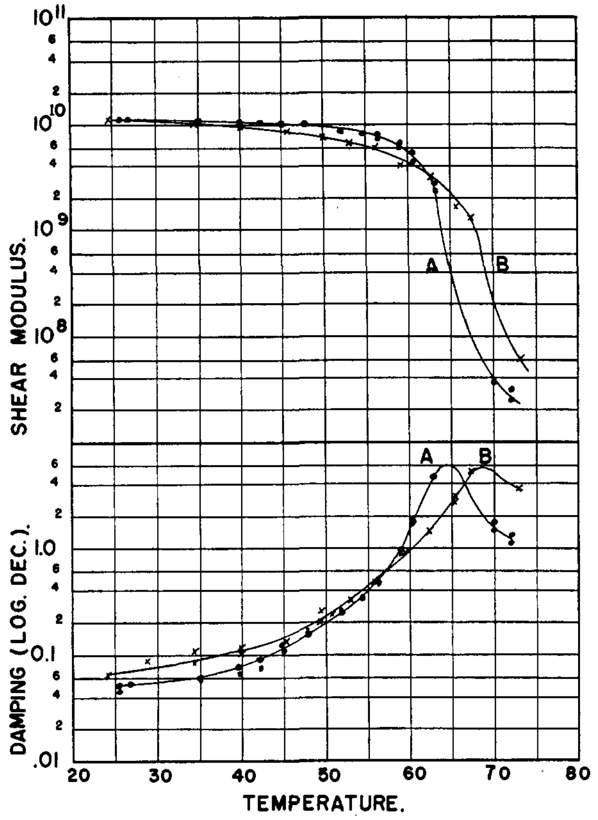

Fig. 1.—Dynamic mechanical properties of styrene–methyl acrylate copolymers: A, homogeneous; B, heterogeneous.

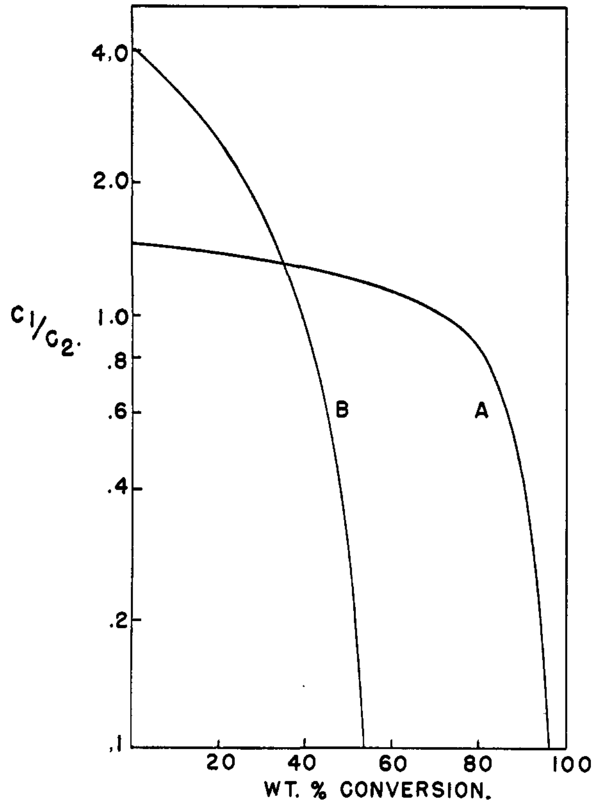

Fig. 2.—Composition ratio of copolymer being formed at any time as a function of degree of conversion: A, styrene/methyl acrylate; B, methyl acrylate/vinyl chloride.

through a maximum. At still higher temperatures the modulus is low, and the damping and modulus again become less temperature dependent. The homogeneous material has a narrower transition range; the damping peak is sharper, and the drop in the modulus is very steep. The transition temperature (here defined as the temperature of maximum damping) is usually a linear function of the corresponding pure polymers.[10] In a homogeneous copolymer, all the molecular segments are in a similar environment and so tend to change from the solid (glass) state to the liquid or rubbery state over a narrow temperature range. The softening range of high polymers is very similar to the melting of crystalline materials in many respects. In the heterogeneous copolymer some of the molecules are rich in the lower "melting" component (methyl acrylate) than others. Figure 2 shows that most of the molecules in the heterogeneous material contain slightly more styrene than the molecules of a homogeneous material, but that 10 to 20% of the molecules are predominantly methyl acrylate. As a result, the transition range is broadened, the damping at 25° is increased because of the few molecules very rich in methyl acrylate, and the transition temperature is raised by the large portion of material containing slightly more styrene than the homogeneous material of the same over-all composition.

Figure 2, which has been constructed from the

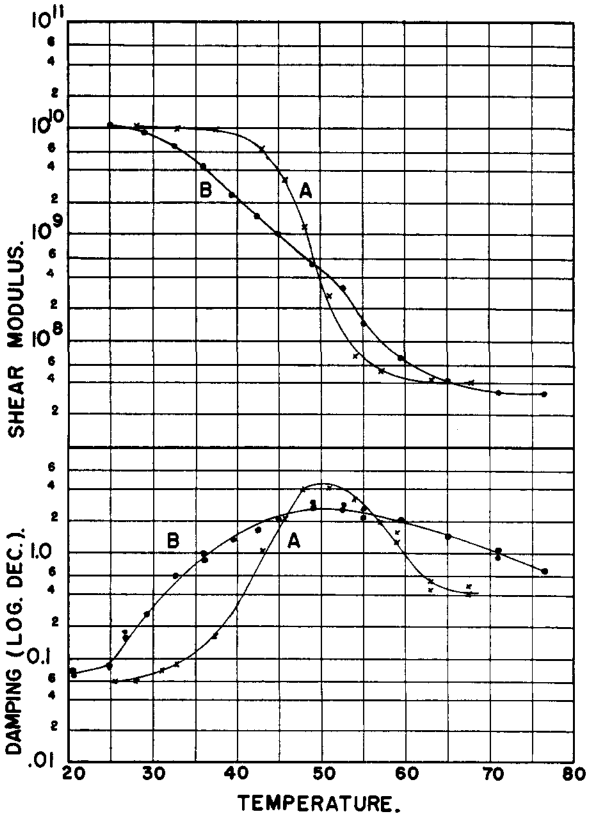

Fig. 3.—Dynamic mechanical properties of vinyl chloride–methyl acrylate copolymers: A, homogeneous; B, heterogeneous.

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[10] L. E. Nielsen, R. E. Pollard and E. M. McIntyre, *J. Polymer Sci.*, **6**, 661 (1951).

published values of the monomer reactivity ratios,[11] indicates that the vinyl chloride–methyl acrylate copolymers tend to be much more heterogeneous than the styrene–methyl acrylate copolymers. The composition remains fairly constant up to 80% conversion for the styrene material, but the composition of the vinyl chloride materials changes greatly with the degree of conversion. The vinyl chloride copolymer is largely methyl acrylate up to about 40% conversion and nearly pure polyvinyl chloride from 60% to 100% conversion. Figure 3 gives data on the vinyl chloride–methyl acrylate copolymers. As in the case of the styrene-containing materials, heterogeneïty broadens the transition range. As expected from their greater heterogeneity, the vinyl chloride polymers are capable of giving the broader transition range as measured by the half-widths of the damping peak or the slope of the modulus curve in the transition region. This is illustrated again in Fig. 4 for the vinyl chloride–β cyanoethoxyethyl acrylate copolymers. The broadening of the transition range shows up in this case in the modulus curves but is not so apparent from the damping curves. The heterogeneous copolymer contains so much of the "low melting" acrylate component that the material becomes soft at a lower than normal temperature. Although the monomer reactivity ratios for this system are not available, it appears the one copolymer is so heterogeneous it has many of the characteristics of a physical mixture of two polymers. The upswing in the damping curves at temperatures above the damping peak is characteristic of the onset of viscous flow[12] and may be the cause of it in this case.

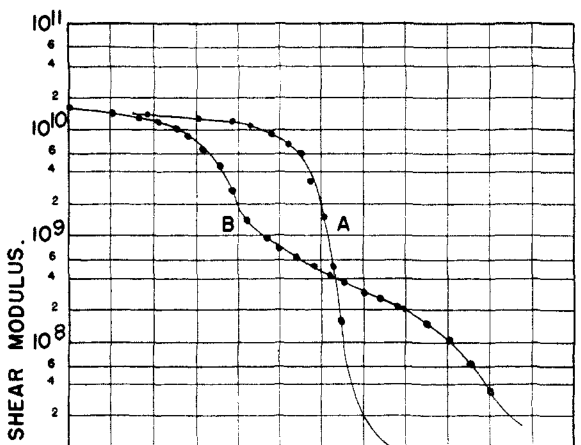

Fig. 4.—Dynamic mechanical properties of vinyl chloride–β-cyanoethoxyethyl acrylate copolymers: A, homogeneous; B, heterogeneous.

The dynamic mechanical properties of a mixture of polyvinyl chloride and a butadiene–acrylonitrile rubber are shown in Fig. 5. The strongly polar nature of these two polymers makes it possible for them to be mutually soluble in one another. The molecular aggregates, if any, must be very small as the material is quite transparent. The dynamic curves are similar to those of a normal polymer or copolymer except the damping peak is much broader and lower, and the modulus decreases gradually over a very wide temperature range. The maximum in damping occurs at a temperature between the corresponding temperatures of the pure components. The soft butadiene–acrylonitrile rubber acts as a plasticizer for the polyvinyl chloride.

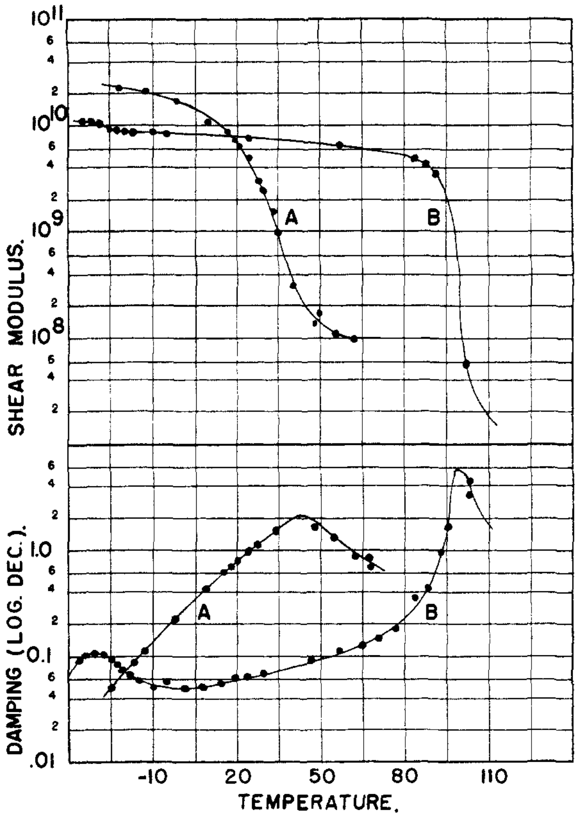

Fig. 5.—Dynamic mechanical properties of polymer mixtures: A, polyvinyl chloride and butadiene–acrylonitrile rubber; B, polystyrene and styrene–butadiene rubber.

Polystyrene and the styrene–butadiene rubber did not form a miscible mixture. Molecular aggregates of considerable size exist in such mixtures as indicated by the milkiness of films of the material. The dynamic mechanical data shown in Fig. 5 substantiate this conclusion. The damping curve has two peaks, and the modulus curve has two inflection points. The low temperature peak

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(11) See reference (1), or E. C. Chapin, G. E. Ham and R. G. Fordyce, THIS JOURNAL, **70**, 538 (1948); F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, *ibid.*, **70**, 1519 (1948).

(12) Unpublished data of Monsanto Chemical Company. See also K. Wolf, *Kunstoffe*, **41**, 89 (1951).

occurs at about the same temperature as for the rubber by itself while the high temperature peak is nearly the same as for pure polystyrene.[7] In such mixtures the rubbery component has very little plasticizing action on the higher "melting" component.

Conclusions

Dynamic mechanical tests are a promising new tool in the study of high polymeric substances for freedom of molecular motion, solubility and molecular aggregation, and chemical heterogeneity. Such measurements, especially the damping, give very sensitive indications of the environment in which the molecular segments find themselves. In this respect the tests are similar to tests of dielectric constant and power factor[13,14] but have the added advantage that they apply to non-polar materials as well as polar ones.

Acknowledgments.—The assistance of Robert Pollard and others on the preparation of the various copolymers was greatly appreciated. The β-cyanoethoxyethyl acrylate copolymers were made by Richard Morner. Leland Child made the viscosity determinations, and Stephania Jaworska made the chlorine analyses. The many discussions with Rolf Buchdahl during the course of this work have been of much assistance.

[13] R. Fuoss, THIS JOURNAL, **61**, 2334 (1939); **63**, 2401, 2410, 2832 (1941).

[14] A. Schallamach, *Trans. Faraday Soc.*, **45**, 605 (1949).

SPRINGFIELD, MASS.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Mechanism of Initiation of Emulsion Polymerization by Persulfate[1]

BY I. M. KOLTHOFF, E. J. MEEHAN AND E. M. CARR

RECEIVED OCTOBER 24, 1952

The rate of disappearance of potassium persulfate has been determined in aqueous solutions containing methanol, ethanol or allyl alcohol in the absence and presence of allyl acetate. Allyl acetate does not affect the initial rate of disappearance of persulfate. Methanol and ethanol cause pronounced increases in the rate, but in the presence of allyl acetate and methanol or ethanol the rate is about the same as in the presence of allyl acetate alone. The results are interpreted on the assumption that persulfate does not react directly with any of the above organic substances but that sulfate free radicals are produced only by thermal dissociation of persulfate. In the absence of allyl acetate the sulfate radical reacts with methanol or ethanol forming a free radical derived from the alcohol. This in turn reacts with persulfate forming another sulfate radical thus leading to chain decomposition of persulfate. In the presence of both allyl acetate and alcohol essentially all the sulfate radicals are captured by allyl acetate and the chain decomposition is prevented.

Introduction

The mechanism of initiation of emulsion polymerization by persulfate is not understood completely. In this paper the question is considered whether the rate of production of sulfate radicals is determined solely by the rate of thermal dissociation of persulfate[2]

$$S_2O_8^{--} \longrightarrow 2SO_4^{-}\cdot \qquad (1a)$$

or whether persulfate also reacts directly with monomer M

$$S_2O_8^{--} + M \longrightarrow {}^{-}SO_4M\cdot + SO_4^{-}\cdot \qquad (2)$$

The reaction between persulfate and allyl acetate has been studied in the absence and presence of simple alcohols. The kinetics of the reaction of persulfate with methanol has been investigated previously by Bartlett and Cotman.[3] The results did not show conclusively whether the primary step was thermal dissociation (reaction 1a) or reaction (1b)

$$S_2O_8^{--} + CH_3OH \longrightarrow SO_4^{-}\cdot + HSO_4^{-} + \dot{C}H_2OH \qquad (1b)$$

According to Bartlett and Cotman[3] the further sequence of reactions is represented by the equations (numbering of equations corresponds to that of Bartlett and Cotman)

$$SO_4^{-}\cdot + CH_3OH \longrightarrow HSO_4^{-} + \dot{C}H_2OH \qquad (4)$$

$$\dot{C}H_2OH + S_2O_8^{--} \longrightarrow HCHO + HSO_4^{-} + SO_4^{-}\cdot \qquad (5)$$

$$2\dot{C}H_2OH \longrightarrow HCHO + CH_3OH \qquad (6)$$

In this paper it has been found that the sulfate radical adds to allyl acetate more quickly than it reacts with an alcohol. From the results it is inferred that the chain reaction between persulfate and alcohols is initiated by sulfate radicals formed in the thermal dissociation of persulfate and not by direct reaction between persulfate and alcohol. Similarly the polymerization of allyl acetate is initiated by sulfate radicals formed by thermal dissociation and not by reaction 2.

Experimental

Materials.—The following liquids were purified by distillation at atmospheric pressure using a 12-inch column packed with glass helices. Allyl acetate: Eastman Kodak Co., b.p. 101–102°; the distillate was acid-free; it was stored in a refrigerator until used. Allyl alcohol: Eastman Kodak Co., b.p. 94–96°; bromometric titration indicated a purity of 99.6%. Ethanol: absolute, commercial grade. Methanol: Baker reagent. Potassium persulfate: Merck analytical reagent, recrystallized; 99.5% pure according to iodometric titration.[4] All other materials were reagent grade chemicals.

Analytical Methods.—In most of the work persulfate was determined by the ferrous iron method in the presence of a large concentration of sodium bromide. A complete description of the determination of persulfate in the presence of organic compounds is to appear elsewhere.[4] Formaldehyde was determined by use of the color reaction with chromotropic acid.[5] Allyl acetate was determined bromometrically.

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[1] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] I. M. Kolthoff and I. K. Miller, THIS JOURNAL, **73**, 3055 (1951).

[3] P. D. Bartlett and J. Cotman, Jr., *ibid.*, **71**, 1419 (1949).

[4] I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, **25**, (1953), in press.

[5] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 400 (1945).