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Formation of Graft Polymers by γ-Irradiation of Natural Rubber Latex and Methyl Methacrylate

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Most previous studies of the polymerization of vinyl monomers in the presence of a pre-formed polymer by γ-irradiation have been concerned with bulk polymerization.[1] The irradiation of natural rubber swollen with methyl methacrylate has been investigated in some detail[2] and the reaction products isolated and characterized. In the present investigation, the effect of γ-irradiation on latices of natural rubber containing methyl methacrylate has been studied. The properties of the resulting graft polymer latices are compared with those of similar latices in which graft polymerization was initiated by redox catalysts.[3]

EXPERIMENTAL

Materials

The natural rubber latex used was an ammonia-preserved centrifuged concentrate of 61.3% total solids and 60.0% dry rubber content. Methyl methacrylate (Kallodoc grade) was obtained from I.C.I., Ltd. In experiments in which polymerization was initiated by irradiation, the methyl methacrylate was freed from inhibitor by washing first with a 10% solution of sodium hydroxide, then with distilled water, and finally drying over sodium sulfate. The hexachloroethane and *tert*-dodecyl mercaptan were commercial samples purified by recrystallization from alcohol and by distillation under reduced pressure, respectively. Other materials used were of laboratory reagent grade.

Polymerization by γ-irradiation

To 117 g. of rubber latex were added 31 g. of a 1.5% (by weight) solution of ammonia followed by 30 g. of methyl methacrylate containing 0.35 g. of oleic acid. This mixture was filtered through muslin to remove any traces of coagulum and transferred to 30 ml. glass tubes with ground glass stoppers, so as to leave an air space of not more than 0.1 ml. in each tube. The latex samples were then exposed, at an ambient temperature of 34°C., to a Co-60 source of nominal uniform field intensity 1.5×10^5 rep/hr. The samples were not agitated during irradiation, and direct comparisons between results were restricted to groups of samples that had been simultaneously exposed.

Polymerization by Redox Catalysts

30 g. of methyl methacrylate containing 0.35 g. of oleic acid and 0.16 g. of *tert*-butyl hydroperoxide was divided into three equal parts which were added, at 1 hr. intervals, to 117 g. of rubber latex diluted with 31 g. of 1.5% ammonia solution. 2.1 ml. of a 10% (by weight) aqueous solution of tetraethylene pentamine, divided into three equal parts, was used to activate the hydroperoxide, one part of the amine solution being added to the latex mixture 10 min. after each addition of methacrylate. After the last addition of tetraethylene pentamine, the reaction mixture was allowed to stand for a minimum of 6 hr. so as to obtain not less than 92% conversion of the methyl methacrylate.

Percentage conversions of monomer in both the irradiated and redox-catalyzed systems were calculated from the total solids contents of the latices before and after polymerization. The total solids content was determined by drying samples of the latex at 60°C. and finally heating to constant weight at 100°C. In a few experiments, where representative samples could not be obtained due to destabilization of the latex, percentage conversions of monomer were obtained by coagulating and drying the entire contents of the reaction tubes.

The gel fraction was defined as the fraction of the latex total solids which would not pass through lens tissue paper after the solids had been heated with benzene (1 g./100 ml.) for 10 days at 60°C. Gravimetric analysis of the filtrate facilitated calculation of the gel fraction by difference.

The swelling index of the gel fraction, i.e., the volume of benzene imbibed per gram of gel was determined gravimetrically.

The uncombined polymethyl methacrylate was estimated by two independent methods. (*1*) The latex total solids were exhaustively extracted with benzene at 60°C. and all the soluble polymer precipitated with excess methanol. The dried precipitate was then immersed in acetone for 10 days at room temperature to extract the uncombined polymethyl methacrylate. The identity of the extract was checked by oxygen analysis using the Unterzaucher method. (*2*) Uncombined polymethyl methacrylate was separated and estimated by the methanol titration method of Merrett.[4]

Viscosity measurements were carried out in benzene solution.

Latex films were prepared by evaporating to dryness a measured amount of the latex on a levelled glass plate, in a slow stream of air at 30°C. The latex was confined to the plate by strips of glass cemented round the edges of the plate.

Vulcanized latex films were obtained by compounding the latex with 1% sulfur, 1% zinc oxide, and 1% zinc diethyldithiocarbamate (calculated on the weight of total polymer), evaporating the film to dryness as above, and finally heating in hot air for 45 min. at 100°C.

RESULTS AND DISCUSSION

Figure 1 shows the rate of polymerization of methyl methacrylate in natural rubber latex when the system was irradiated as described above. After a variable induction period of a few minutes (due presumably to small amounts of oxygen in the latex), the reaction rate increased rapidly to give 93% conversion of monomer after 5 hr. irradiation. Addition of hexachloroethane to the latex monomer mixture, which increases the rate of polymerization by γ-radiation of styrene dissolved in dry rubber, did not affect significantly the rate of polymerization in the present experiments.[5] Polymerization was retarded, however, by *tert*-dodecyl mercaptan and zinc dibutyl dithiocarbamate (ZBC) which are soluble in the disperse phase of the latex, and even more strongly by sodium diethyldithiocarbamate (SDC) which is soluble in the latex serum (Fig. 1). For purposes of comparison, a latex methyl methacrylate mixture of the same initial composition as that of latex A in Figure 1 was polymerized using *tert*-butyl hydroperoxide and tetraethylene pentamine as catalyst, without irradiation until the conversion of monomer was 93% (latex R). This latex and those irradiated in the absence of dithiocarbamates, possessed greater colloidal stability than the latices irradiated in the presence of SDC or ZBC.

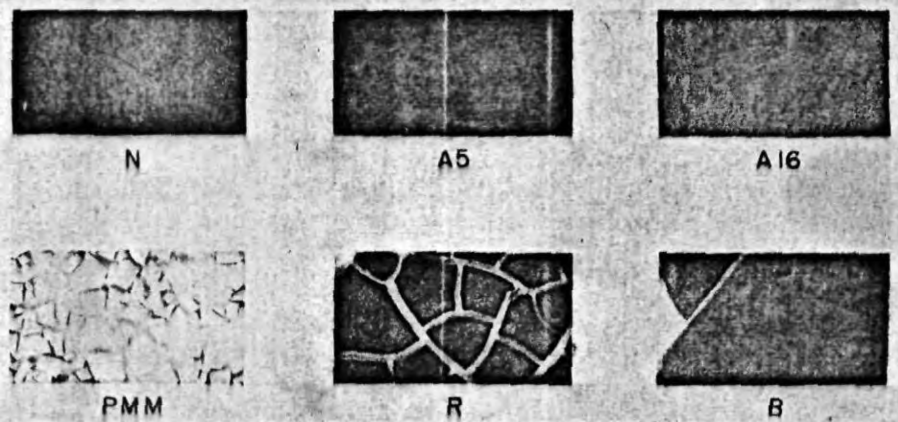
N
A5
A16
PMM
R
B

Fig. 1. Film forming characteristics of latices. N, R, A5, A16, and B are dried latices of composition shown in Table I. PMM is dried polymethyl methacrylate latex.

Polymer characterization measurements on latices A and B (Fig. 1) and latex R gave the results shown in Table I. A5 and A16 refer to latex A after irradiating for 5 hr. and 16 hr., respectively.

A5 contains a higher ratio of grafted polymer to homopolymer than product R, and the molecular weight of the homopolymer is greater in A5. The large increase in the proportion of homopolymer after 16 hr. irradiation is attributed to chain scission of the grafted polymethacrylate chains,[6] an explanation which is supported by the decrease in molecular weight of the homopolymer. The relatively high gel content and low swelling index in

TABLE I
Polymerization of Methyl Methacrylate in Natural Rubber Latex: Polymer Characterization Data

Latex	Exposure, hr.	Gel, %	Swelling index, ml./g.	Total PMM content, % of total solids	Homopolymer PMM content, % of total PMM	[η] of homopolymer g.$^{-1}$ ml.
N[a]	0	21	111	—	—	—
R	0	25	116	28.0	40	58.7
A5	5	42	56	28.5	28	101.0
A16	16	68	38	28.8	74	84.1
B	5	37	60	26.7	70	58.9

[a] Unmodified natural rubber latex.

benzene of the A5 polymer, compared with product R, is due to radiation-induced crosslinking of the rubber. The retardation in rate of polymerization caused by *tert*-dodecyl mercaptan, and the high proportion and low molecular weight of the homopolymer in product B (Table I), are both consistent with the occurrence of chain transfer reactions in the presence of this mercaptan.

Latex Film-Forming Properties

One of the most striking differences between the natural rubber-methyl methacrylate latices polymerized by irradiation and those prepared by hydroperoxide-tetraethylene pentamine initiation is that the former latices can be dried to give continuous films even when the polymerized methacrylate content is as high as 30% of the weight of the dry product. The latices obtained using the above redox initiator, on the other hand, form discontinuous, cracked films if the polymerized methacrylate content exceeds about 15%, the precise figure depending on the conditions of drying. These differences are illustrated in Figure 1 which shows the continuous films obtained by drying latices A5 and A16 and the severely cracked film obtained from latex R, all three latices containing substantially the same amount of polymerized methacrylate (28%). Similarly, when the three latices were compounded with vulcanizing ingredients, dried, and cured at 100°C., continuous vulcanized films were obtained from latices A5 and A16, but not from latex R. The A5 and A16 vulcanized films possessed a much higher modulus of elasticity and a slightly higher tensile strength than similarly vulcanized films of natural rubber latex itself, but the latter possessed the higher ultimate elongation.

Locus of Polymerization

The results in Table I show that the marked differences in film-forming properties between latices R and A5 or A16 cannot be due to differences in the ratio of grafted polymethyl methacrylate to homopolymer, nor does it appear that the molecular weight of the polymerized methacrylate is a factor of major importance (*vide infra*). Although the percentage of gel polymer is greater in A5 and A16 than in latex R, this would not be expected to facilitate film formation. Indeed, it is known that the introduction of crosslinks, *e.g.*, by sulfur prevulcanization of natural latex, tends to have the opposite effect.

Since film formation requires, at some stage of drying, cohesion between the individual latex particles, it is likely that the surface properties of the particles are of particular importance. This suggests that the difference in film-forming properties between latices R and A5 or A16 is due primarily to a difference in the *distribution* of polymerized methacrylate throughout the latex particles, a higher proportion of the polymerized methacrylate being located in the surface regions in latex R. It is apparent from Figure 1 that the discontinuous latex R film resembles in structure the dried polymethyl methacrylate latex more closely than do the A5 and A16 films.

In the preparation of the A5 and A16 products, it is assumed that the high penetrating power of the γ-radiation results in the formation of free radicals (capable of initiating polymerization) uniformly throughout each methacrylate swollen rubber particle. The radiation also produces free radicals in the aqueous phase of the latex, and some of these radicals may be expected to diffuse to the surface and initiate graft or homopolymerization predominantly in the surface regions of the particles. According to these views, the presence of polymerization retarders, such as *tert*-dodecyl mercaptan or ZBC which are soluble in methacrylate swollen rubber particles but insoluble in water, should give a product in which an increased proportion of the polymerized methacrylate is located in the surface regions of the particles. Conversely, the presence of water-soluble polymerization retarders such as SDC should give a product in which the polymerized methacrylate is distributed essentially uniformly throughout the latex particles. Figure 1 shows that the presence of *tert*-dodecyl mercaptan did indeed result in a product (latex B) which gave a cracked film on drying, although the film-forming properties of this latex were better than those of latex R. It may be seen from Table I that this difference between latices B and R cannot be due to a difference in the molecular weight of the polymerized methacrylate, since this is essentially the same in the two products.

The preparation of dried films from the latices irradiated in the presence of ZBC or SDC was difficult, because of their colloidal instability. However, when the latex containing ZBC was acidified, the polymer was not precipitated as a compact coagulum but as large floccules, indicating that the cohesion on acidification between the particles of this latex was weaker than between the particles of latex A5 or A16, which gave compact coagula on acidification. The addition of acid to the polymethyl methacrylate latex itself caused the precipitation of polymer in the form of finely divided floccules. These results support the view that a higher proportion of the polymerized methacrylate was located at the surface of the particles in the latex containing ZBC than in latex A5 or A16. As expected, the latex containing SDC gave a firm coagulum when acidified, but this result is *probably not significant since nearly* 40% of the methyl methacrylate was not polymerized (Fig. 2).

In the preparation of latex R, initiation of polymerization is due to free radicals produced by the interaction of *tert*-butyl hydroperoxide dissolved in the methacrylate swollen rubber particles and tetraethylene pentamine in the aqueous phase of the latex. With such a hydrophobic-hydrophilic catalyst combination, it is probable that most of the initiating free radicals are formed near the surface of the latex particles and, because of the high viscosity of the rubber phase, initiate polymerization mainly in the region where they are formed. It follows that the use of a catalyst system which is soluble only in the disperse phase of the latex should lead to a more uniform distribution of polymerized methyl methacrylate throughout the rubber particles, to give products with better film-forming properties than latex R. Work to be published shortly[7] describes the preparation of such products with benzoyl peroxide and dimethyl aniline as catalyst. It is concluded, therefore, that the distribution of a polymerized monomer such as methyl methacrylate within the individual particles of natural latex is a factor of major importance in determining the film-forming characteristics and colloidal behavior of the latex. The principles discussed here should be relevant to many emulsion copolymerization reactions in which the composition of the copolymer changes with percentage conversion of the

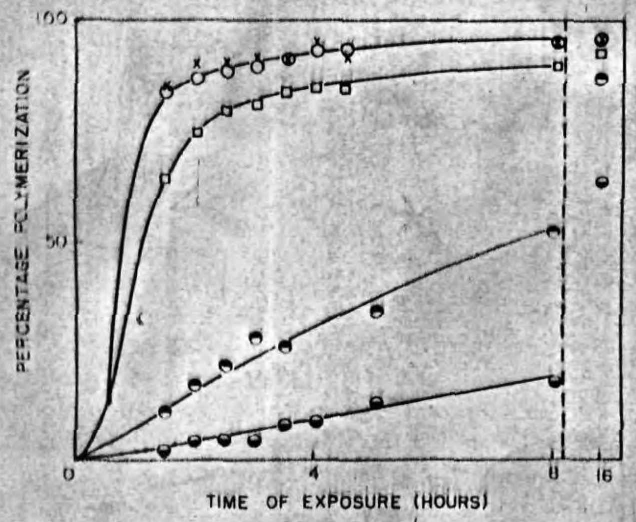

Fig. 2. *Effect of additives on rate of polymerization of methyl methacrylate in hevea* latex. (○) No additive; (×) 2% hexachloroethane, on monomer; (□) 2% *tert*-dodecyl mercaptan, on monomer; (◓) 1% zinc dibutyldithiocarbamate, on monomer; (◒) 1% sodium diethyldithiocarbamate, on monomer.

monomer, particularly when the emulsion copolymer particles approach in size those of natural rubber latex.

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Synopsis

Exposure of mixtures of natural rubber latex and methyl methacrylate to γ-radiation from a Co-60 source results in polymerization of the methyl methacrylate to give a mixture of the homopolymer and grafted polymer. The ratio of grafted polymer to homopolymer and the molecular weight of the homopolymer are both considerably higher than in similar systems where polymerization was initiated by a redox catalyst. The ability of the irradiated latices to form continuous films on drying is much greater than that of corresponding redox-polymerized systems. This difference is attributed primarily to the location of the polymerized methyl methacrylate throughout the individual latex particles, the polymerized methacrylate being more uniformly distributed in the case of the irradiated latex. Use of polymerization retarders which are soluble in methyl methacrylate swollen rubber supplies evidence that an increased proportion of the polymerized methacrylate is located in the surface regions of the latex particles. Conversely, a more uniform distribution of the polymer is obtained by the use of water-soluble retarders. The probable significance of these results in relation to emulsion copolymer systems is pointed out.

Résumé

On a exposé des mélanges de caoutchouc naturel et de méthacrylate de méthyle aux radiations γ d'une source de Co-60. Il en est résulté une polymérisation du méthacrylate de méthyle. On a obtenu un mélange de polymère greffé et d'homopolymère. Le rapport polymère greffé-homopolymère et le poids moléculaire sont tous deux considérablement plus élevés que dans des systèmes similaires polymérisés par initiation redox. La capacité des réseaux irradiés à former des films continus par séchage est également beaucoup plus grande que dans les systèmes redox correspondants. On attribue cette différence en premier lieu à la situation du polyméthacrylate de méthyle à travers les particules de latex. Le polyméthacrylate de méthyle est réparti plus uniformément dans le cas du réseau iradié. On a pu montrer en utilisant des retardateurs de polymérisation solubles dans le caoutchouc gonflé de méthacrylate de méthyle qu'une proportion plus grande de méthacrylate polymérisé était située en surface des particules de latex. Au contraire, en utilisant de retardateurs soluble dans l'eau, on a obtenu une distribution plus homogène du polymère. On note en plus la signification probable de ces résultats en relation avec les systèmes de copolymérisation en émulsion.

Zusammenfassung

Die Bestrahlung einer Mischung von Naturkautschuklatex und Methylmethacrylat mit der γ-Strahlung einer Co-60 Quelle führt zur Polymerisation des Methylmethacrylats unter Bildung einer Mischung des Homopolymeren und des Propfpolymeren. Sowohl das Verhältnis des Propfpolymeren zum Homopolymeren als auch das Molekulargewicht des Homopolymeren sind beide beträchtlich höher als bei Anregung der Polymerisation mit einem Redoxkatalysator in ähnlichen Systemen. Die Fähigkeit der bestrahlten Latices, beim Trocknen zusammenhängende Filme zu bilden, ist viel grösser als die der entsprechenden Systeme bei Redoxpolymerisation. Dieser Unterschied wird primär auf die Verteilung des polymerisierten Methylmethacrylats in den einzelnen Latexpartikeln zurückgeführt, wobei im Falle der bestrahlten Latices das polymerisierte Methylmethacrylat gleichmässiger verteilt ist. Durch Verwendung von Polymerisationsverzögerern, die in der Methylmethacrylat-Kautschukquellung löslich sind, werden Hinweise dafür erhalten, das ein gesteigerter Anteil des polymerisierten Methylmethacrylats sich im Oberflächenbereich der Latexpartikel befindet. Umgekehrt wird bei Verwendung wasserlöslicher Verzögerer eine einheitlichere Verteilung des Polymeren erhalten. Auf die Bedeutung, die diese Ergebnisse für Emulsionscopolymerisationssysteme haben können, wird hingewiesen.

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