Polybutadiene Hydroperoxide by Singlet Oxygen: Its Grafting and Morphology in Polystyrene Matrix

F. M. PENG, *Monsanto Polymer Products Company, Springfield, Massachusetts*

Synopsis

Singlet oxygen was used to synthesize hydroperoxide functional groups onto a polybutadiene. These hydroperoxides served as grafting sites for the preparation of polybutadiene-modified polystyrene by a bulk polymerization process. As anticipated, the dispersed polybutadiene droplet size decreased as the level of hydroperoxidation increased. Various types of morphology, similar to those of butadiene–styrene diblock and styrene–butadiene–styrene triblock copolymer systems, were obtained. Furthermore, at an extremely high level of hydroperoxidation, a unique reticular structure of polybutadiene was developed.
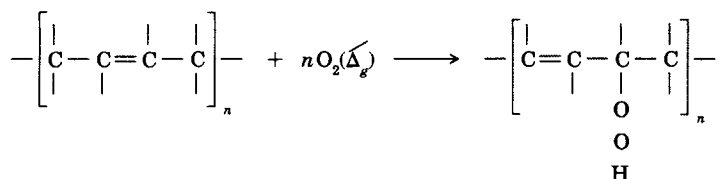
INTRODUCTION

In polymeric systems containing two immiscible phases of the oil-in-oil emulsion, three parameters generally determine the dispersed droplet sizes[1-10]: (1) viscosities of the dispersed and the continuous phases, (2) stress forces acting upon the dispersed droplets, and (3) the interfacial tension of the droplets.

The dispersed droplet size is known to influence the fracture mechanics, the melt rheology, and surface phenomena, etc., of the polymer system. The influence of the fine detail of the droplet internal structure is not well documented, although theoretically it can be predicted to affect physical properties, such as the balance of impact strength and tensile modulus. Thus, the importance of knowledge about dispersed phase morphology cannot be overemphasized.

In high impact polystyrene thermal polymerization, the styryl radicals abstract the allylic hydrogens from the polybutadiene, and styrene grafting commences.[11-13] As the polymerization proceeds, the polybutadiene phase precipitates as droplets from the mixture. The styrene graft chains act to reduce the interfacial tension of the dispersed polybutadiene droplets, and also stabilize the polybutadiene particles to form the oil-in-oil emulsion, comprehensively described by Molau et al.[14-18] Thus, one would expect the dispersed droplet size to be reduced when the graft level is increased. In addition, the density and the relative length of the graft chains are important molecular parameters in determining dispersed phase morphology.

Over a very broad range not achievable by conventional approaches, this study investigated the morphology impelled by the interfacial tension using singlet oxygen to graft the polybutadiene.

Singlet oxygen reacts with polybutadiene or unsaturated polymers to form polymeric hydroperoxides:

$$-\left[\begin{array}{c}|\\C\\|\end{array}-\begin{array}{c}|\\C\\|\end{array}=\begin{array}{c}|\\C\\|\end{array}-\begin{array}{c}|\\C\\|\end{array}\right]_n + nO_2(\Delta_g) \longrightarrow -\left[\begin{array}{c}|\\C\\|\end{array}=\begin{array}{c}|\\C\\|\end{array}-\begin{array}{c}|\\C\\|\\O\end{array}-\begin{array}{c}|\\C\\|\end{array}\right]_n$$
$$O$$
$$H$$

and is considered to initiate the photooxidation of unsaturated polymers.[19-41] However, De Paoli and Schultz[42] have shown that it is free radicals, but not singlet oxygen, that initiate the process.

During the mass polymerization, these hydroperoxides, serving as grafting sites, effectively increase the graft level and allow manipulation of the morphology of the dispersed polybutadiene phase.

Singlet oxygen can be generated by various methods. For this study, the decomposition of the triphenyl phosphite–ozone adduct[43-49] was used:

$$(\Phi O)_3 P \; + \; O_3 \; \xrightarrow{-78°C} \; (\Phi O)_3 PO_3 \; \xrightarrow{-35°C} \; (\Phi O)_3 PO \; + \; O_2(\Delta_g)$$
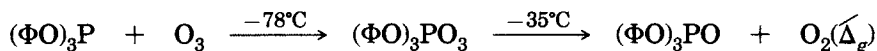
In addition to the interest of singlet oxygen in polymers as described above, it also plays very important roles in biology.[50-52]

EXPERIMENTAL

Materials

The polybutadiene used was Diene 55NFA, made by Firestone Synthetic Rubber and Latex Co., having $M_w = 237,000$ and $M_n = 104,000$. Ozone was generated from a Welsbach T-23 ozone generator, using dry air from Matheson Co. Triphenyl phosphite was from Eastman Kodak Co.; styrene monomer, from Monsanto Co. All materials were used, as received, without further purification.

Triphenyl Phosphite-Ozone Adduct For Singlet Oxygen

The adduct was prepared by the Thompson method[43] in CH_2Cl_2 to insure formation of the 1:1 adduct of triphenyl phosphite with ozone.[44]

Hydroperoxidation of Polybutadiene

About 14 g of polybutadiene were dissolved in 150 mL of CH_2Cl_2 and cooled to $-78°C$. The triphenyl phosphite–ozone adduct solution at $-78°C$ was added to this cold polybutadiene solution and mixed by agitation and nitrogen bubbling. The mixture was then removed from the cold bath and allowed to warm up to room temperature[19] overnight, generating singlet oxygens to react with the polybutadiene.

The hydroperoxidized polybutadiene was then precipitated by addition of methanol to the solution, and the CH_2Cl_2 was removed under vacuum. This vacuum distillation at room temperature made the polybutadiene very porous and easy to dry. Finally, the precipitated porous hydroperoxidized polybutadiene was dried overnight in vacuum at room temperature with

nitrogen purge. This dried hydroperoxidized polybutadiene was kept under nitrogen at room temperature in the dark.

The presence of —OOH on the polybutadiene was confirmed by reaction with KI in saturated acetone solution[19] to yield the yellow iodine. However, quantitative determination for the hydroperoxide was not performed.

Grafting of the Hydroperoxidized Polybutadiene and Its Morphology

Five percent by weight of the polybutadiene was dissolved in styrene monomer purged with nitrogen. A 50 mL Pyrex glass centrifuge tube containing three 0.5 in stainless steel balls was filled halfway with this rubber solution, while being swept with nitrogen to exclude air. The tube was then capped, clamped to a rotator, and the solution was polymerized thermally in an oil bath at 130°C.

Agitation was achieved solely by the steel balls rolling up and down as the rotator turned at about 3 rpm. The dispersed polybutadiene particle size was reproducible with this method of agitation. However, it was only satisfactory for low polybutadiene concentration, due to the high viscosity of the system and the limited agitation by the falling steel balls.

Polymerization was carried beyond phase inversion[10] to about 25% conversion. This partially polymerized "prepoly" syrup was cooled to room temperature, transferred to glass tubes, and sealed under nitrogen. Finally, the polymerization was completed at 150°C for 24 h without agitation. The polymer was then analyzed for the dispersed phase morphology by electron microscopy, using the OsO_4 fixation and ultra thin section technique of Kato.[53]

Determination of Polybutadiene Graft Level

The polymer or the prepoly syrup was dispersed in a 50/50 by volume of MEK/DMF mixed solvent and ultracentrifuged to separate the dispersed gel phase from the matrix phase. The polystyrene in the supernatent liquid was removed and retained for molecular weight measurement, while the gel phase was extracted once more with the solvent and then with methanol. Finally, the methanol was removed and the gel was dried in vacuum with nitrogen purge; the graft level was calculated by the weight of the isolated dried gel. This gel probably included some of the free polystyrene within the polybutadiene particles as well as the chemically grafted polystyrene.

Polystyrene Molecular Weight

The polystyrene was recovered from the supernatent liquid by precipitating in methanol and vacuum drying with nitrogen purge. The specific viscosity was measured in toluene at 25°C and 0.2 g/dL of polystyrene, and the weight average molecular weight $(\overline{M}_w)$ was calculated from the following relationships[54,55]:

$$[\eta] = \frac{1}{C} \left[2(\eta_{sp} - \ln \eta_r)\right]^{1/2} \left(1 - \frac{\eta^2_{sp}}{12}\right)$$

$$\log \overline{M}_w = 2.71 + 1.37 \log[\eta]$$

where $[\eta]$ is intrinsic viscosity, η_{sp}, specific viscosity, $\eta_r = 1 + \eta_{sp}$, and C, polymer concentration.

RESULTS AND DISCUSSION

Singlet Oxygen Hydroperoxidized Polybutadiene

This hydroperoxidized polybutadiene appeared stiffer than the original one, and its degree of stiffness increased with the —OOH level. Regular polybutadiene dissolves readily in styrene monomer overnight at room temperature. However, the hydroperoxidized polybutadiene took much longer to dissolve, depending on its —OOH level. It is speculated that hydrogen bonding was responsible for these phenomena.

The hydroperoxidized polybutadiene was not very stable in the presence of styrene monomer. Over a period of days at room temperature, polymerization was evidenced, indicating the possible cleavage of the —OOH induced by styrene monomer. This is similar to the hydroperoxy catalysts which likewise exhibit induced decomposition at moderate temperature in the presence of monomers.[56,57] The fact that the singlet oxygen hydroperoxidized polybutadiene did dissolve in styrene monomer proved that it was not crosslinked.

Polymerization

As expected, the styrene polymerization rate and the polybutadiene graft level increased with the —OOH level while the polystyrene molecular weight decreased (Table I).

Morphology

Preliminary investigation with a highly hydroperoxidized polybutadiene (sample A, Table I) showed some interesting results. Five percent of this polybutadiene in styrene monomer was polymerized along with a control of regular polybutadiene (sample C, Table I) at 130°C in sealed glass tubes

TABLE I
Preliminary Results

Sample	Hypothetical (mol —OOH/ mol rubber)[a]	Poly-time at 130°C (min)	Conv. (%)	Matrix polystyrene ($M_w \times 10^{-4}$)	Rubber Graft[b] (%)
A	338.0	60	33	—	—
B	6.78	59	14.5	26.6	55
C	0	70	15.3	27.2	40.4

[a] Assuming 100% efficiency for the preparation of the adduct and the hydroperoxidation of the rubber.

[b] As % of rubber.

without agitation for an hour to 33% conversion. The tubes were then cooled and cut open for vigorous agitation with a spatula. Then they were resealed and polymerized to completion at 150°C. The polymer of the control sample C was opaque, as expected, but that of sample A was transparent. Electron micrographs showed that sample A did not have spherical rubber particles as the control but formed a unique reticulated cylindrical structure of about 0.05 μm in diameter (Figs. 1 and 2). Neither the polymer of sample A nor its prepoly syrup (33% conv), whether agitated or unagitated, was dispersible in MEK/DMF solvent. This indicated that the reticulated polybutadiene became entangled to the extent that it was not dispersible. However,
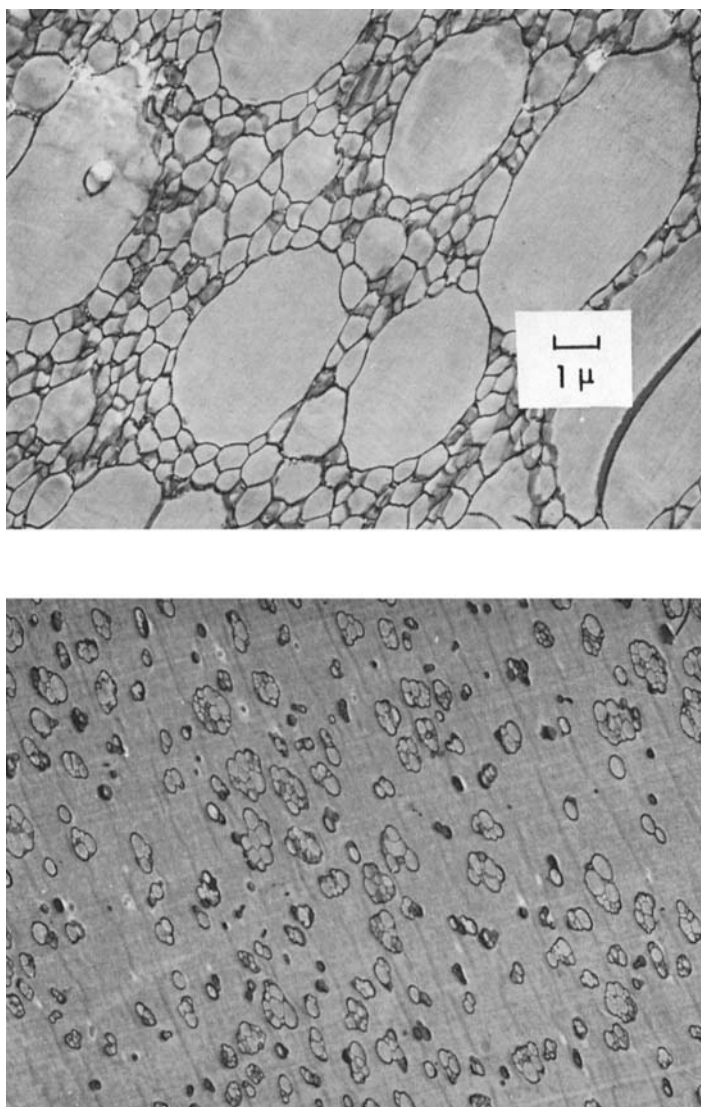
Fig. 1.   Regular rubber: (top) not agitated; (bottom) agitated.
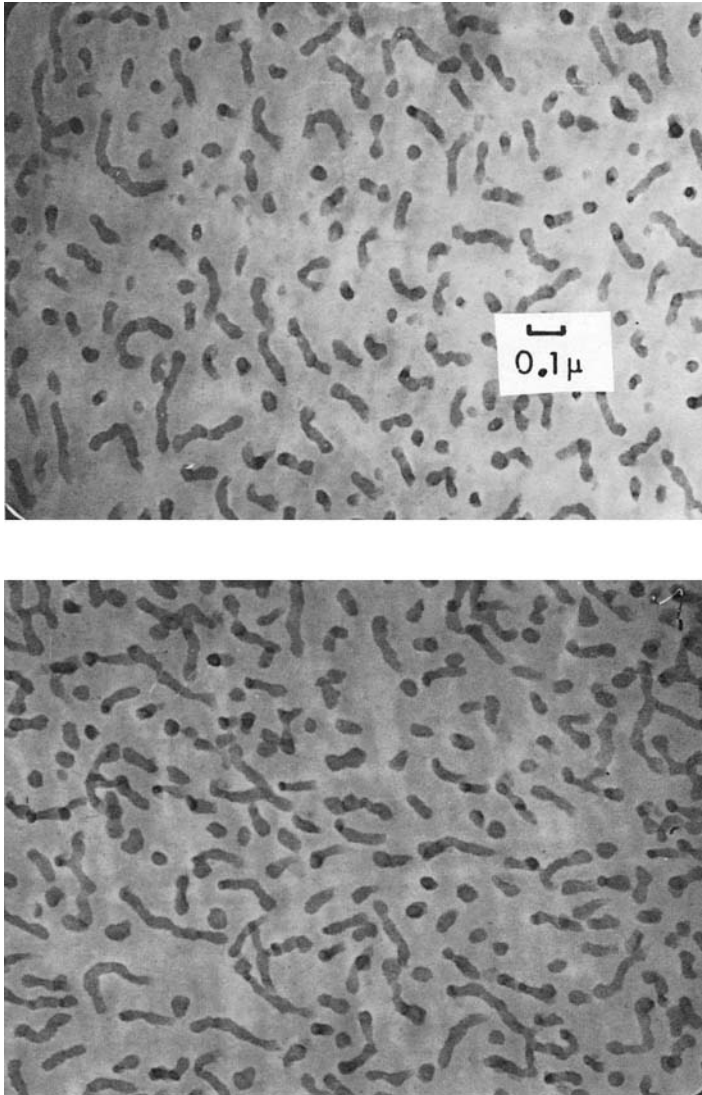
Fig. 2.   Highly hydroperoxidized rubber (338 hypothetical mol—OOH/mol rubber): (top) not agitated; (bottom) agitated.

its prepoly syrup at 33% conv was completely soluble in toluene, indicating that it was not crosslinked at that stage.

When a polybutadiene hydroperoxidized to a much lesser degree (45.2 hypothetical mol —OOH/mol polybutadiene) than sample A was polymerized under agitation in the rotating glass tube with steel balls, it again resulted in a transparent MEK/DMF nondispersible polymer similar to sample A.

Subsequent experiments were carried out with low —OOH levels, by either a low level of hydroperoxidation or a blending of a highly hydro-

peroxidized polybutadiene (45.2 hypothetical mol—OOH/mol polybutadiene) with the regular polybutadiene. The results are summarized in Table II and illustrated with micrographs. The fact that Figures 4 and 5 are quite similar indicates that homogeniety of hydroperoxide distribution on the polybutadiene backbone is not a prerequisite.

Echte et al.[58-60] showed various rubber phase morphologies of styrene–butadiene diblock and triblock systems in polystyrene. Five types of structure were observed. With increasing block styrene content, they are multiple inclusions, protuberant particles, single inclusion, cylinder, and small droplets. The rubber phase morphology was influenced not only by the graft level or the polystyrene block content but also by the matrix molecular weight. It was demonstrated that the morphology could be shifted forward to the high polystyrene block content type by increasing the polystyrene inclusions, through using matrix polystyrene of shorter chain length than the block polystyrene to attain compatibility. On the other hand, it also could be shifted backward to the low polystyrene block content type by reducing the effective block rubber content, through blending with a butadiene homopolymer. Again, homogeniety is not a prerequisite.

Independently, Kruse[61] reviewed the formation of various rubber phase structures and showed the morphology of rubbers in polystyrene. The same five types of morphology were also obtained from styrene–butadiene block copolymers and butadiene homopolymers.

In the above-mentioned works, various chain lengths of butadiene homopolymers and its styrene block copolymers were used. In this study, a single butadiene homopolymer was used to evaluate the effect of grafts on morphology by varying the graft density without being confounded by the variation of the chain length of the polybutadiene.

Basically, all of those five types of morphology were obtained but occurred

TABLE II
Sample Description and Results

Hypothetical (mol —OOH/mol rubber)	Rubber phase particle size $(\mu)^a$	Remarks	Figures
0	1.6	Control, regular rubber	3
2.26	1.6	Blend of high —OOH and regular rubber	4
2.72	1.2	Homogeneously hydroperoxidized rubber	5
4.94	0.97	Homogeneously hydroperoxidized rubber	6
6.78	0.24	Blend of high —OOH and regular rubber	7
11.3	0.19	Blend of high —OOH and regular rubber	8

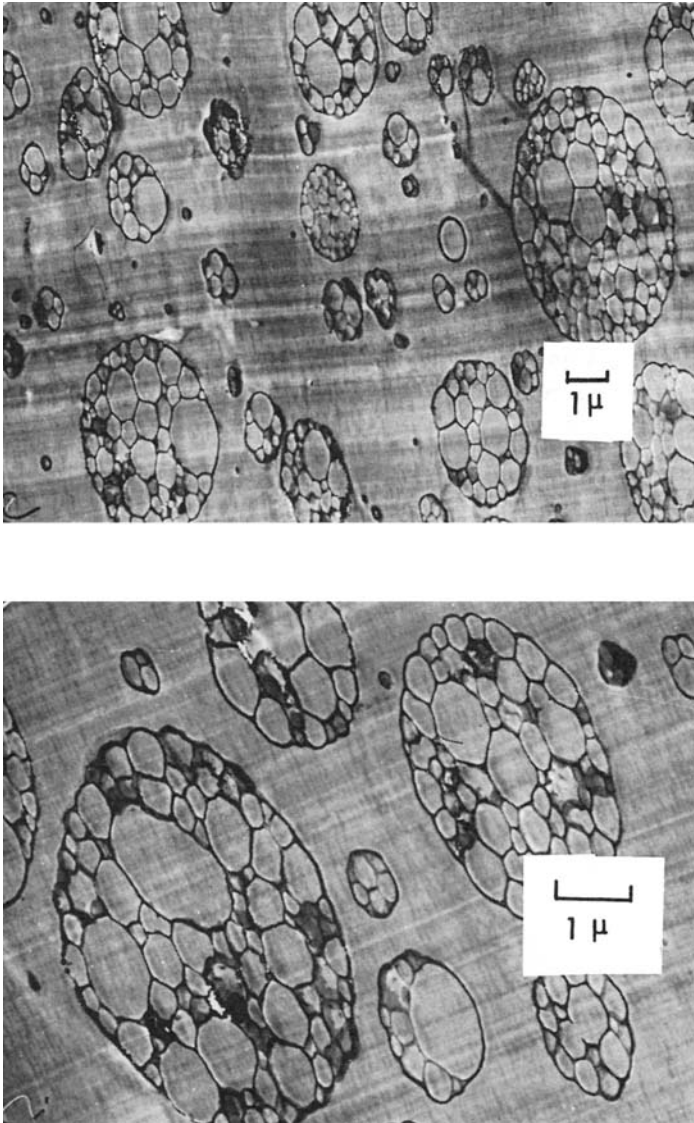^{a} Number average of ca. 50 particles from electron micrographs.

Fig. 3.   Regular rubber system.

in a different sequence. Starting at the low graft level, the familiar type of multiple inclusions was observed (Figs. 3–5), then the single inclusion (Fig. 5–7), the protuberant particles (Figs. 7–9), and finally the unique cylindrical reticulum of the very high graft level (Fig. 3). Note that the protuberant particles were not seen following the type of multiple inclusion as in Echte's work, but at a higher graft level. The small droplets were seen with the protuberant particles before the cylindrical type was devel-
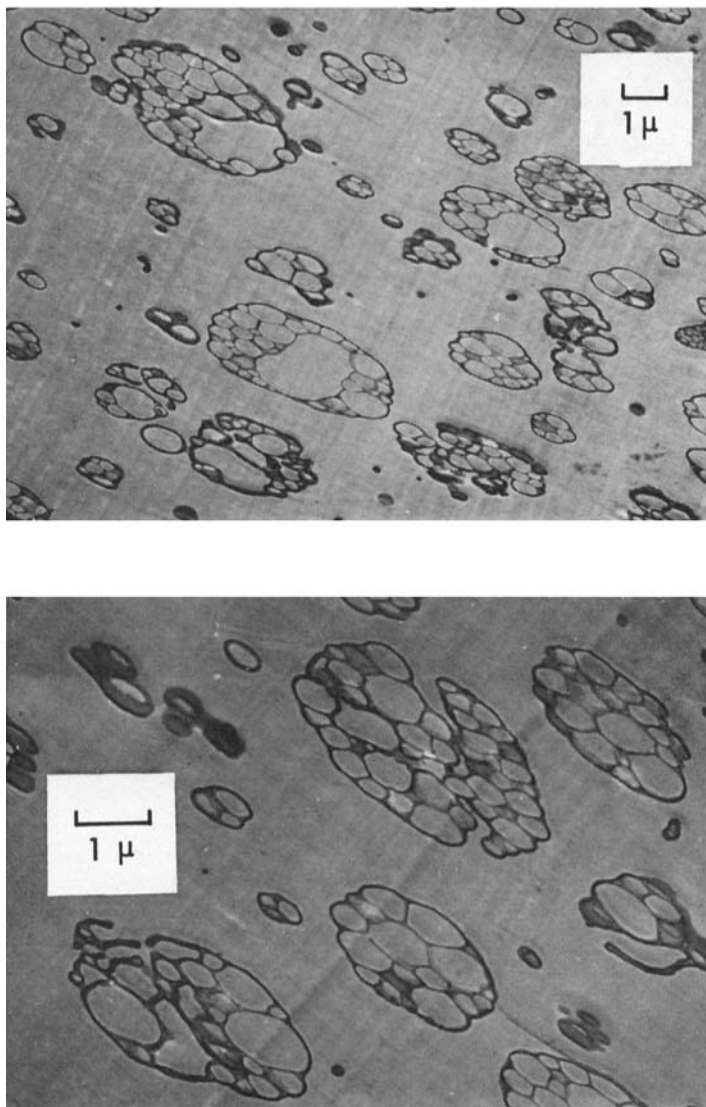
Fig. 4. Hopothetical 2.26 mol —OOH/mol rubber system.

oped. Finally, the cylindrical type evolved, but, as previously described, it was entangled in a reticulum. However, the distinctive features of the lamella and the interpenetrated surface boundary, observed in the butadiene–styrene butadiene triblock copolymer system,[56,60] were not attained.

When the reticulated polybutadiene prepoly syrup (21% conv from the 45.2 hypothetical mol —OOH/mol polybutadiene) was redissolved in styrene monomer with the regular polybutadiene (at 15:85 weight ratio of
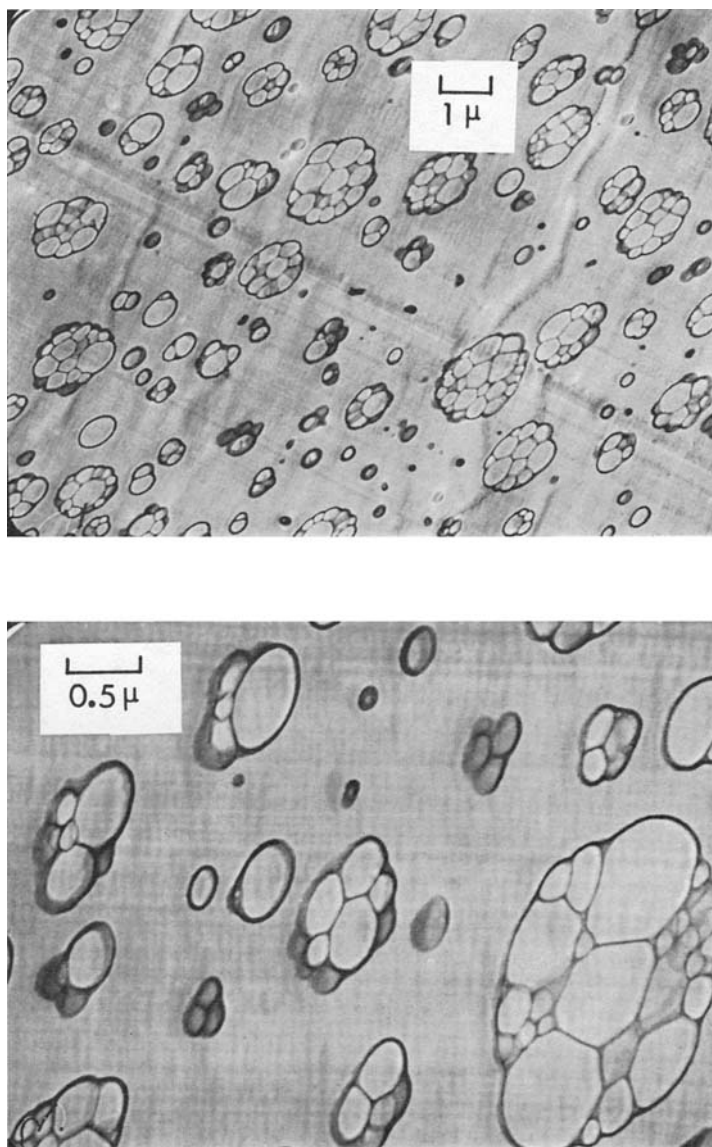
Fig. 5.   Hypothetical 2.72 mol —OOH/mol rubber system.

polybutadienes) and polymerized over again without —OOH, small droplets
were formed (Fig. 9). Moreover, the very highly grafted polybutadiene was
not compatible with the regular polybutadiene and formed its own distinc-
tive domain of small droplets. Yet the statistically less grafted portion must
be compatible with and incorporated into the regular polybutadiene and
resulted in the protuberant particles instead of the multiple inclusion type
of the regular polybutadiene.
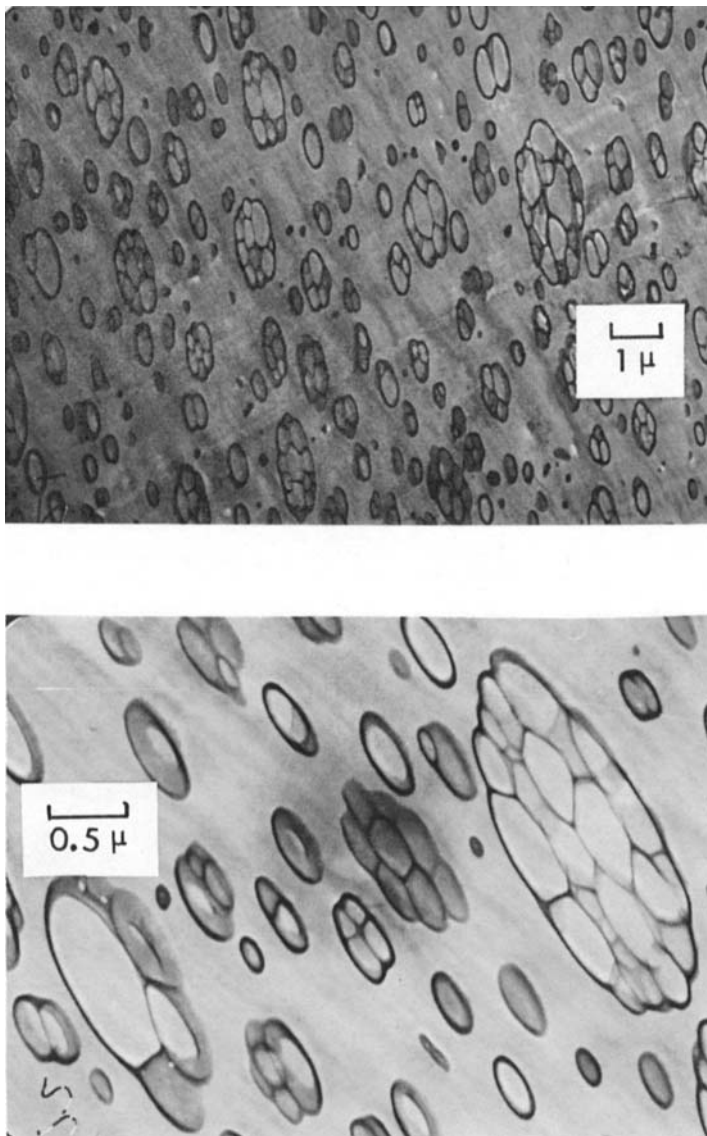
Fig. 6. Hypothetical 4.94 mol —OOH/mol rubber system.

CONCLUSIONS

Attachment of hydroperoxides onto polybutadiene to provide sites for a broad range of grafting was accomplished effectively with singlet oxygen. As a consequence, these phenomena happened:

1. With an increasing hydroperoxide level, the amount of grafting increased and the polybutadiene phase droplet size decreased.
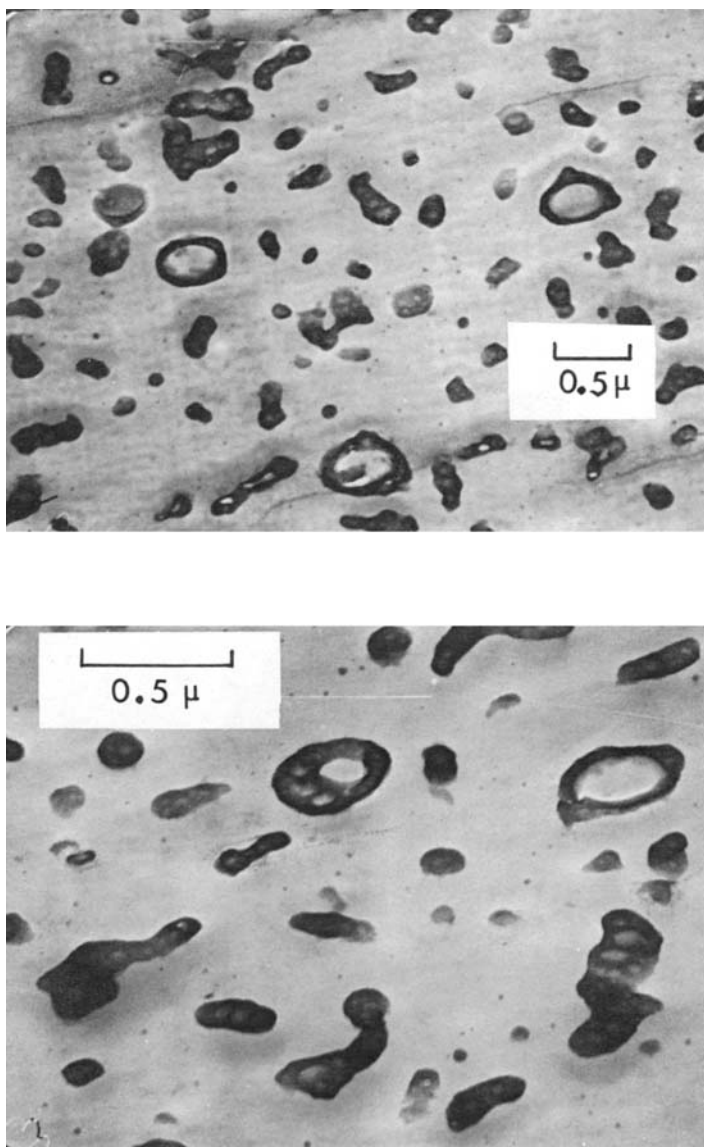
Fig. 7. Hypothetical 6.78 mol —OOH/mol rubber system.

2. With heavy grafting of butadiene homopolymer, various rubber phase morphologies similar to those of styrene–butadiene diblock and styrene–butadiene–styrene triblock copolymers were obtained.

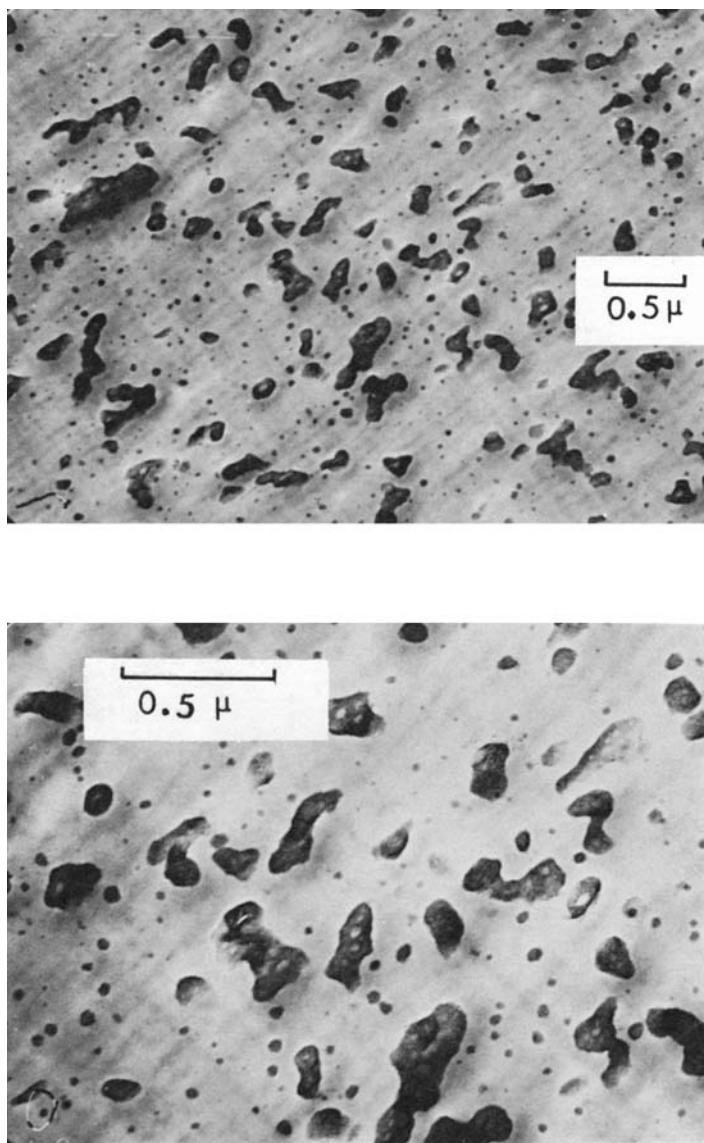3. At extremely high graft level, a unique reticular structure of polybutadiene was developed.

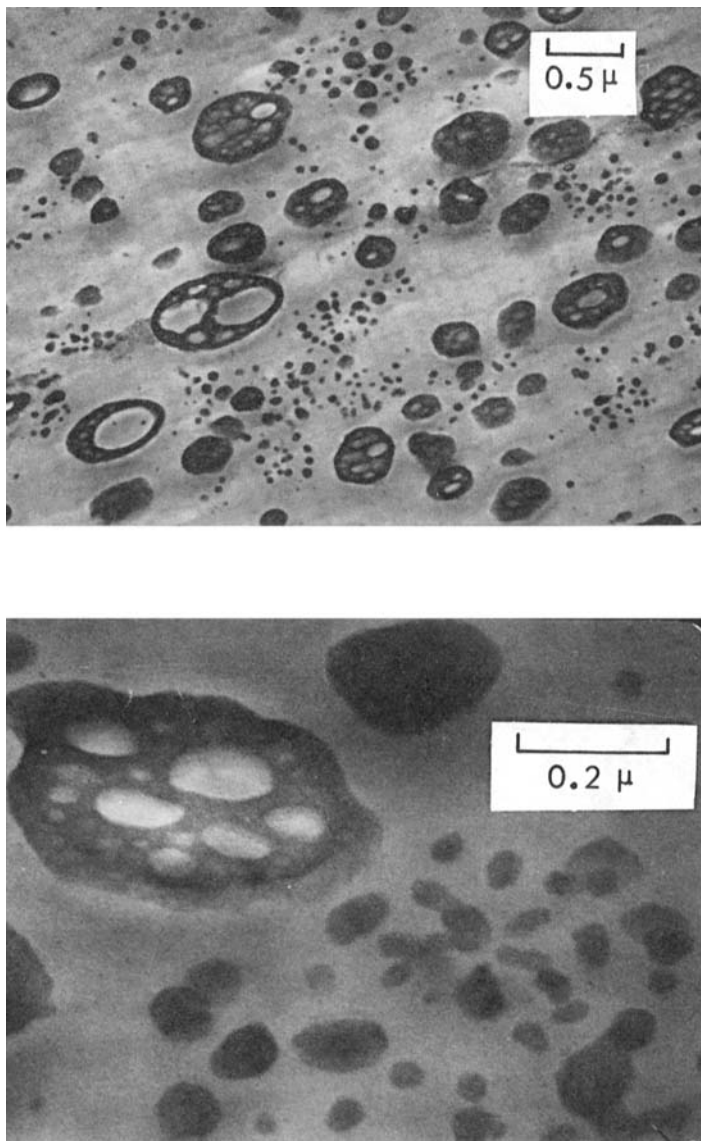Fig. 8. Hypothetical 11.3 mol —OOH/mol rubber system.

Fig. 9. Regular rubber with highly grafted rubber system.

References

1. G. F. Freeguard, *Polymer*, **13**, 336 (1972).
2. G. F. Freeguard, AIChE Annual Meeting Paper No. 34-E, New York, Nov. 1972.
3. D. P. Kessler and J. L. York, *AIChE J.*, **16**(3), 369 (1970).
4. F. Ide and I. Sasaki, *Chem. High Polym.*, **27**, 617 (1970).
5. F. B. Sprow, *AIChE J.*, **13**(5), 995 (1967).
6. H. J. Karam and J. C. Bellinger, *Ind. Eng. Chem. Fundam.*, **7**, 576 (1968).
7. G. I. Taylor, *Proc. Roy. Soc. London*, **A146**, 501 (1934).
8. S. Tomotika, *Proc. Roy. Soc. London*, **A150**, 322 (1935).
9. J. O. Hinze, *AIChE J.*, **1**, 289 (1955).

10. C. B. Bucknall, *Toughened Plastics,* Applied Science, Essex, United Kingdom, 1977, Chap. 4.

11. G. D. Ballova, V. M. Bulatova, K. A. Vylegzhanina, Ye. I. Yegorova, L. L. Sul'zhenko, and G. P. Fratkina, *Polym. Sci. USSR,* 11(8), 2080 (1969).

12. F. M. Merrett, *Trans. Faraday Soc.,* 50, 759 (1954).

13. J. A. Blanchette and L. E. Neilsen, *J. Polym. Sci.,* 20, 317 (1956).

14. G. E. Molau, *J. Polym. Sci., Part A,* 3, 1267 (1965).

15. G. E. Molau, *J. Polym. Sci., Part A,* 3, 4235 (1965).

16. G. E. Molau and H. Keskkula, *J. Polym. Sci., Polym. Chem. Ed.,* 4, 1595 (1966).

17. G. E. Molau and W. M. Wittbrodt, *Macromolecules,* 1(3), 260 (1968).

18. G. E. Molau and H. Keskkula, *Appl. Polym. Symp.,* 7, 35 (1968).

19. M. L. Kaplan and P. G. Kelleher, *J. Polym. Sci., Polym. Chem. Ed.,* 8, 3163 (1970).

20. M. L. Kaplan and P. G. Kelleher, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.,* 11(2), 731 (1970).

21. M. L. Kaplan and P. G. Kelleher, *Rubber Chem. Technol.,* 45(2), 423 (1972).

22. G. P. Canva and J. J. Canva, *Rubber J.,* 153(9), 36 (1971).

23. A. K. Breck, C. L. Taylor, K. E. Russell, and J. K. S. Wan, *J. Polym. Sci., Polym. Chem. Ed.,* 12(7), 1505 (1974).

24. J. K. Rabek and B. Ranby, *J. Polym. Sci., Polym. Chem. Ed.,* 14(6), 1463 (1976).

25. V. B. Ivanov and V. Ya. Shlyapintokh, *J. Polym. Sci., Polym. Chem. Ed.,* 16(5), 899 (1978).

26. A. Zweig and W. A. Henderson, Jr., *J. Polym. Sci., Polym. Chem. Ed.,* 13(3), 717 (1975).

27. H. C. Ng and J. E. Guillet, *Macromolecules,* 11(5), 923 (1978).

28. C. Tanielian and J. Chaineaux, *J. Photochem.,* 9(1), 19 (1978).

29. D. J. Carlsson and D. M. Wiles, *Rubber Chem. Technol.,* 47(4), 991 (1974).

30. A. Zweig and W. A. Henderson, Jr., *J. Polym. Sci., Polym. Chem. Ed.,* 13(4), 993 (1975).

31. D. J. Carlsson, T. Suprunchuk, and D. M. Wiles, *J. Polym. Sci., Polym. Lett. Ed.,* 14(8), 493 (1976).

32. B. Ranby and J. F. Rabek, *Am. Chem. Soc., Symp. Ser.,* 25 (*Ultraviolet Light Induced React. Polym., Int. Symp., 1975*), 391 (1976).

33. B. Ranby and J. F. Rabek, *Singlet Oxygen Reactions with Organic Compounds and Polymers,* Wiley, New York, 1978.

34. J. F. Rabek, J. Y. Shur, and B. Ranby, *Singlet Oxygen React. Org. Compd. Polym., Pap. EUCHEM Conf., 1976,* 264 (1978).

35. J. F. Rabek, G. Ramme, G. Canback, B. Ranby, and V. T. Kagiya, *Eur. Polym. J.,* 15, 339 (1979).

36. J. F. Rabek and B. Ranby, *Photochem. Photobiol.,* 28, 557 (1978).

37. J. F. Rabek and B. Ranby, *Photochem. Photobiol.,* 30, 133 (1978).

38. J. F. Rabek and B. Ranby, *J. Appl. Polym. Sci.,* 23, 2481 (1979).

39. J. F. Rabek, J. Lucki, and B. Ranby, *Eur. Polym. J.,* 15, 1089 (1979).

40. M. A. Golub, Pure Appl. Chem., 52, 305 (1980).

41. D. Lala and J. F. Rabek, *Eur. Polym. J.,* 17, 7 (1981).

42. M. A. De Paoli and G. W. Schultz, *Polym. Bull.,* 8, 437 (1982).

43. Q. E. Thompson, *J. Am. Chem. Soc.,* 83, 845 (1961).

44. R. W. Murray, J. W. P. Lin, and M. L. Kaplan, *Prepr. Ann. N.Y. Acad. Sci.,* 171, 121 (1970).

45. R. W. Murray, W. C. Lumma, Jr., and J. W. P. Lin, *J. Am. Chem. Soc.,* 92, 3205 (1970).

46. R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.,* 90, 537 (1968).

47. R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.,* 91, 5358 (1969).

48. P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N.Y. Acad. Sci.,* 171, 79 (1970).

49. M. E. Brennan, *Chem. Commun.,* 946 (1970).

50. N. I. Krinsky, in *Singlet Oxygen,* H. H. Wasserman and R. W. Murray, Eds., Academic, New York, 1979, Chap. 12.

51. I. Matsuo, K. Yoshino, and M. Ohkido, *Curr. Probl. Dermatol.,* 11, 135 (1983).

52. A. V. Starostin, I. B. Fedorovich, and M. A. Ostrovskii, *Biofizika,* 29(2), 344 (1984).

53. K. Kato, *J. Electron Microsc. (Jpn.),* 14(3), 220 (1965).

54. T. D. Varma, & M. Sengupta, *J. Appl. Polym. Sci.,* 15, 1599 (1971).

55. Von J. W. Breitenback and H. Gabler, *Makromol. Chem.,* 37, 53 (1960).

56. C. Walling and L. Heaton, *J. Am. Chem. Soc.,* 87, 38 (1965).

57. S. W. Benson, *J. Chem. Phys.,* **40**, 1007 (1964).

58. A. Echte, *Angew. Makromol. Chem.,* **58**(846), 175 (1977).

59. A. Echte, *Angew. Makromol. Chem.,* **90**(1417), 95 (1980).

60. F. Haaf, H. Breuer, A. Echte, B. J. Schmitt, and J. Stabenow, *J. Sci. Ind. Res.,* **40**, 659 (1981).

61. R. L. Kruse, Pap. Meet. Am. Chem. Soc., Div. Org. Coat. Plast. Chem., New Orleans, LA, March 20–25, 1977.