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1963

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Abstract

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PHYSICAL CHEMISTRY

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MOLECULAR MOBILITIES IN LATEXES

STUDIED BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

(Presented by Academician V. A. Kargin on 10 V 1963)

It is known that the properties of polymers are determined not only by their chemical nature, but also by structural features (crystallinity, orientation, etc.). The physical state of a polymer largely determines the rate and direction of various kinetic processes occurring in the substance.

Polymers in the form of aqueous dispersions find wide application in various fields of technology. Natural and synthetic latexes are one representative of this class of compounds. The polymer in a latex is present in the form of separate particles (globules), surrounded by a layer of emulsifying substances that impart hydrophilicity to the polymer molecules of rubber; as a result, the colloidal system as a whole acquires great stability. The dispersion medium also contains stabilizers, antioxidants, and other compounds necessary for imparting special properties to latex as a colloidal system (⁀1). The properties of products made from latexes are determined mainly by the type of polymer, although the inevitable multicomponent nature of the initial latex will always affect the properties of the finished films (⁀2).

Of particular interest is the study of the properties of the polymer itself in latex, where it is present in the form of globules. Apart from the early studies of Kemp (⁀3) and Hauser (⁀4), carried out on natural latex, there are very few data in the literature concerning the nature, shape, and sizes of globules. But even these data do not reveal the physical state of the polymer in the globule.

In the present work we studied the proton-resonance spectra of several latexes, since it is known that the phenomenon of nuclear magnetic resonance depends substantially on the mobility of nuclei (⁀5).

Method. The proton magnetic-resonance spectra were recorded on a KIS-25 spectrometer (25 MHz). All measurements were carried out at room temperature. For latexes and solutions, spherical ampoules were used (diameter 3 and 5 mm; resolution about 1 Hz). The NMR spectra of films were recorded in the following way: 1) by the high-resolution method with the use of a superstabilizer. The absorption functions $f(H)$ were recorded at a rate of $\sim$ 5 Hz per second. In this case cylindrical ampoules were used (volume $\sim$ 0.1 cm^3), with

Fig. 1. Proton resonance spectra of (a) natural latex and (b) a film made from natural latex. The chemical shift is measured relative to latex water in millionths of the applied field (ppm).

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a resolution of about 2 Hz. The signal was recorded over a range of about 0.3 oersted. The zero values of $f(H)$, necessary for measuring the line width at half-height $\Delta H_{1/2}$, were estimated by switching on, at the corresponding edges of the sweep, a current shifting the field H_0 by another 0.2 oersted in the required direction. 2) With the use of low-frequency signal modulation at 30 Hz and subsequent synchronous detection (recording df/dH and measuring the width of the maximum slope δH). Because there was no rotation, the field inhomogeneity worsened to $2 \div 3 \cdot 10^{-6}$. In all cases the modulation amplitude was chosen from the condition $H_{\text{mod}} = {}^1/_5 \div {}^1/_6\, \delta H$. When recording the NMR spectra of latexes, chemical shifts were measured relative to the water signal in millionths of the applied field (ppm) by the usual side-band method. When method 1) was used, orientational measurements of δ were carried out with the stabilizer switched on by the substitution method (accuracy ± 0.2 ppm). It turned out that the chemical

the shifts of the rubber protons in the latex and in the film are, within the limits of experimental error, the same (the same also applies to mixtures of latexes with low-molecular solvents).

Results and discussion. The following latexes were studied in this work: natural latex Revertex (dry matter content 30%), butadiene-styrene SKS-30 (dry matter content 30%), and polychloroprene (nairit L-4). Latex films were obtained by drying under conditions of equilibrium with atmospheric humidity.

Fig. 1. Proton resonance spectra of (**a**) natural latex and (**b**) a film made from natural latex. The chemical shift is measured relative to latex water in millionths of the applied field (ppm).

The spectra of natural-rubber latex NR and of the corresponding film are shown in Fig. 1. The narrow intense line (not shown in full) is due to the water of the latex. The line width from water for SKS-30 and nairit latexes practically does not exceed the instrumental width, while for NR it is somewhat higher—2.2 Hz—which is probably due to the greater viscosity of the dispersion medium in the case of NR. The broad line in the spectrum (Fig. 1*a*), due to the CH_2, CH_3 protons of the rubber, is shifted by 3.1 ppm into stronger fields relative to water. Measurement of $\Delta H_{1/2}$ of the rubber line was carried out by resolving the total signal into signals from the water protons and from the polymer protons. Accurate measurements are very difficult because of the strong influence of the tuning of the signal phase and of the signal from the substance in the capillary

through which the sphere is filled.

Table 1

Widths of the proton-resonance lines of rubber in latexes, mixtures of latexes with solvents, and rubber films, and chemical shifts of the principal rubber signal relative to latex water

Parameters	NR Revertex	Butadiene-styrene SKS-30	Polychloroprene nairit
$\Delta H_{1/2}$ (in latex)	$0.034 \pm 3\%$	$0.019 \pm 18\%$	$0.035 \pm 20\%$
$\Delta H_{1/2}$ (in film)	$0.085 \pm 10\%$	$0.28 \pm 20\%$	$0.195 \pm 10\%$
ΔH (in film)	$0.083 \pm 10\%$	$0.33 \pm 20\%$	$0.09 \pm 10\%$
$\Delta H_{1/2}$ (in latex with addition of 5% CCl_4)	$0.019 \pm 5\%$	$0.017 \pm 10\%$	$0.032 \pm 10\%$
$\Delta H_{1/2}$ (in latex with addition of 10% benzene)	$0.018 \pm 5\%$	–	–
δ, chemical shift (ppm relative to H_2O)	3.10 ± 0.20	3.20 ± 0.20	3.20 ± 0.20

Table 1 gives data on $\Delta H_{1/2}$ of the rubber protons and on the chemical shifts of the principal polymer signal in latexes and their mixtures with low-molecular solvents, CCl_4 and benzene. The same table also gives data on the widths of the lines from rubber protons in the film, obtained by methods 1) and 2).

From a comparison of the widths of the signals from rubber protons in the film and in the latex, it is seen that in all cases the line width in the film is greater than in the latex. Such narrowing must be associated with an increase in molecular mobility. For polymer chains, the principal mechanism responsible for line narrowing is segmental motion [(6)]. Thus, the potential barrier for segmental motion is lowered when the polymer is in the form of latex globules.

The increase in molecular mobility in latexes apparently refutes the approximate notion of globules as particles of polymer

(of the same structure as in the bulk), surrounded by a layer of emulsifier. Although the globules are in continuous Brownian motion, the frequencies of this motion are not high and cannot effectively influence the rate of magnetic relaxation. It is more natural to suppose that the mobility of the chains increases

as a result of penetration into the globules of low-molecular components, in the present case emulsifier and water. According to Kemp' s data [3], the amount of water (for NR) present inside the globules may reach 10-15%. In the course of the experiments it was also observed that, during film formation, the narrow line from water in the NMR spectrum disappears rapidly; at the same time the rubber line broadens, reaching a maximum value (~ 0.08 Oe) upon prolonged drying.

Confirmation of this point of view is also provided by the data on $\Delta H_{1/2}$ in mixtures of latexes with solvents. In this case the NMR lines become still narrower. However, the line-narrowing effect in the latex-solvent composition will largely be determined by the type of solvent and polymer. In contrast to NR, for other types of rubber the narrowing effect does not exceed the error limits (solvent CCl_4).

Table 2

Chemical shifts δ of rubber protons (relative to $CHCl_3$) in CCl_4 solutions (in ppm)

Type of rubber	Protons: CH_3	Protons: $-CH_2-$	Protons: $-CH_2-C=$	Protons: $-CH=$	Protons: ring protons
Natural rubber	5.60 ± 0.1			2.40 ± 0.1	
SKS-30		5.48 ± 0.08		2.11 ± 0.1	0.28 ± 0.18
Polychloroprene		5.10 ± 0.08		1.95 ± 0.08	

Table 2 gives data for high-resolution spectra of rubber solutions in CCl_4 (2-5%) with $CHCl_3$ used as an internal standard. A further decrease of $\Delta H_{1/2}$ in polymer solutions makes it possible to separate individual lines from the CH_2, $-CH=$, and other groups. The chemical shifts in Table 2 for NR (groups CH_2, CH_3) and for polychloroprene (CH_2, $-CH_2-CHCl=$) are given taking into account the overlap of nearby signals. The data for NR agree with results reported earlier [7]. The line widths from the $CHCl_3$ standard reflect the degree of hindrance of segmental motion in dilute solutions (about 10 Hz).

In the case of polychloroprene, displacement of the chemical shifts of the protons of the $-CH_2-$ and $-CH=$ groups into weaker fields occurs as a result of replacement of one of the protons at the double bond by a chlorine atom.

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Received
8 IV 1963

REFERENCES CITED

1. J. Noble, *Latex in Technology*, 1962.

2. S. S. Voyutskii, B. A. Shtarkh, *Physicochemistry of the Processes of Film Formation from Aqueous Dispersions of High Polymers*, 1954.

3. A. R. Kemp, *Rubber Chem. and Technol.*, **11**, 394 (1938).

4. E. Hauser, *Latex*, 1932.

5. E. Andrew, *Nuclear Magnetic Resonance*, IL, 1957.

6. A. Odajama, *J. Phys. Soc. Japan*, **14**, 777 (1959).

7. H. S. Gutowsky, A. Saika et al., *J. Chem. Phys.*, **27**, 534 (1957).

Note: Figure translations are in progress. See original paper for figures.