which all possible hydrogen bonds are made intermolecularly between predominantly extended chains.[12] A number of slight modifications of these extended chain structures involving less coiling as compared to the polypeptides and proteins have been postulated for certain members of the nylon family.[13] Contact angle results may help to distinguish between these structures.

Summary and Conclusions

A drop-solvent-casting method which required the use of minute amounts of sample and solvent was devised to form very thin polyamide films on platinum sheets. Such films were suitable, as prepared, for both contact angle and MAIR ir spectroscopic measurements. MAIR spectroscopy, sensitive to monolayer levels of contamination, also was used to validate the preparative and cleaning procedures. When cast from dichloroacetic acid, nylon 11, nylon 6, and polyglycine all exhibited wetting behavior similar to that reported earlier by Ellison and Zisman and verified here. This wetting behavior is different from that regularly found with nonamide polymers in that (a) contact angle values plot as two separate and nearly parallel straight lines in graphs of cos θ *vs.* γ_{LV}, one line characterizing hydrogen-bonding liquids and the other nonhydrogen-bonding liquids, and (b) these lines intercept the cos $\theta = 1$ axis to give higher critical surface tension intercepts which range from 40 to 50 dyn/cm. It is proposed that these wetting features may be exploited as diagnostic indicators of the presence of accessible hydrogen-bonding sites at a polymer surface. A systematic variation in the slopes of the contact angle graphs appears to be additionally useful as an indicator of the relative proportion of these surface sites. Formic acid-cast films of nylon 11 and nylon 6 do not show the dual wettability feature, presumably because of polymer fractionation, configuration, or crystallinity changes which remain to be identified. MAIR spectroscopy is not as sensitive to differences in casting solvent as contact angle measurements. These data encourage similar investigations of more complex polypeptides[14] and eventually of complex biological macromolecules themselves.

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Notes

Diffusion of Radioactively Tagged Small Molecules through Biaxially Stretched Rubbers

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The question of whether local molecular mobility in rubbery polymers is affected by large deformations is important in interpreting viscoelastic properties of such materials subjected to large strains.[1,2] For example, natural rubber and butyl rubber were studied by Mason[1] with superposition of small oscillating deformations in extension on large static tensile strains; and a styrene–butadiene rubber was studied by Smith and Dickie[2] with stress–strain measurements at different strain rates in uniaxial extension up to high elongations. From both investigations, it was deduced that the monomeric friction coefficient depends very little on the uniaxial extension ratio up to moderate-to-high values (2, 6, and 6, respectively, for natural, butyl, and styrene–butadiene rubber). Of course, the behavior can be expected to depend on the degree of cross-linking and other factors.

Another gauge of local mobility can be obtained from the diffusion of a radioactively tagged small molecule (*i.e.*, molecular weight of the order of 200) in trace amounts through the polymer.[3–5] The translational friction coefficient of the penetrant, obtained from the diffusion coefficient, can be closely correlated with the monomeric friction coefficient of the polymer itself in many cases. In the present note, the effect of large static strain on the diffusion coefficient on *n*-hexadecane (HXD) and 1,1-diphenylethane (DPE) in several rubbery polymers is reported.

The penetrants, tagged with ^{14}C, have been described in previous publications.[4,5] The rubber samples—natural rubber (NR), styrene–butadiene rubber (SBR), and *cis*-polybutadiene (PB-*cis*)—were cross-linked by dicumyl peroxide; they are identified by code numbers which correspond to previous reports,[5,6] except for PB-*cis* 116-150, which has a somewhat higher degree of cross-linking[7] than the polybutadiene PB-*cis* 116-30 investigated earlier.

Biaxial stretching was performed by clamping a disk-shaped sample in the jig shown in Figure 1, without the cell base. An expandable rubber plug was temporarily placed in the middle of the plunger assembly

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TABLE I
DIFFUSION COEFFICIENTS AT 25°

Penetrant	Polymer	Code	$(R'/R)^2$	h/h'	Log D'	Log D
HXD	NR	109-B$_2$-75[a]	1.54	1.54	−7.19	−7.15
			6.00	6.10	−7.14	−7.15
DPE	NR	109-B$_2$-40[b]	6.53	6.56	−7.24	−7.26
DPE	SBR	93-20[c]	8.82	8.82	−7.71	−7.69
DPE	PB-*cis*	116-150	2.63	2.71	−6.43	−6.40

[a] Identified in ref 6. [b] Identified in ref 4 and 6. [c] Identified in ref 4 and 9.

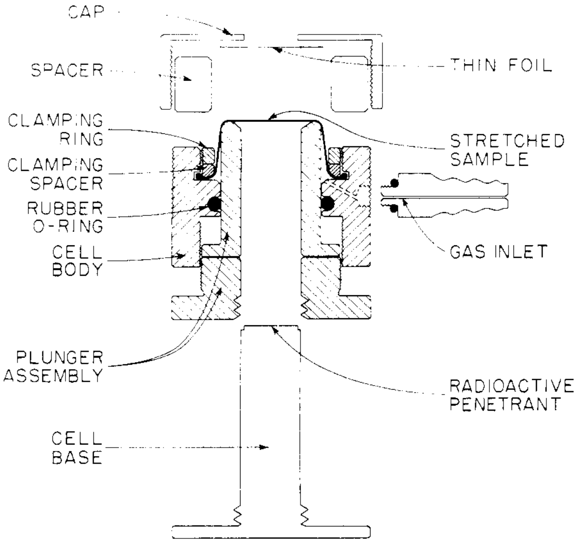

Figure 1. Device for biaxial stretching of a disk-shaped rubber sample and subsequent diffusion measurements by the thin smear method.

and nitrogen was forced under pressure through the gas inlet, while a plastic cap on top prevented the sample from stretching too far. Finally, the plunger assembly was raised to the desired position, the pressure was slowly released, and the expandable plug was removed. The thicknesses h and h', before and after stretching, were measured by placing a hollow cylinder with a fiducial mark (not heavy enough to cause perceptible deformation) on the rubber disk while it was supported from below; a travelling telescope was focussed on the fiducial mark. The relative lateral dimensions of a grid marked on the flat surface, R and R', were also measured; $(R'/R)^2$ agreed well with h/h' within the uncertainty of measurement, as shown in Table I. The initial thickness h was 1–2 mm. Further details are reported elsewhere.[8]

For measurement of the diffusion coefficient, the thin smear method was employed as described previously,[3–5] placing the cell base shown in Figure 1 in contact with the lower surface of the rubber, and mounting a Geiger-Müller tube above the upper surface. Thus the diffusion took place perpendicular to the two stretch directions. The diffusion coefficient (based on the stretched dimensions, of course) was obtained by curve matching as described in ref 4, taking the absorption coefficient[9] of the β radiation from ^{14}C as 0.34 cm^2/mg. The experiment required from 2 to 9 hr (for one thicker sample, 17 hr); comparatively little stress relaxation would be expected on the basis of viscoelastic measurements.[6,7,10] All measurements were made at 25°.

The results are shown in Table I. The primed symbols refer to the stretched state. The units of the diffusion coefficient D are cm^2/sec. The uncertainty is estimated to be 0.02 in log D' (stretched samples), somewhat larger than the usual estimate of 0.005 for log D (unstretched). It is evident that there is no effect of biaxial elongation, up to a stretch ratio of nearly 3 in each direction, within experimental uncertainty on the diffusion coefficient in the direction normal to stretch and hence on the translational friction coefficient of the penetrant in this direction. This conclusion is consistent with the deductions from viscoelastic measurements cited above,[1,2] although the latter were concerned with uniaxial elongation.

Somewhat different results have been reported by Zakharov[11] for diffusion of tagged polyisoprenes of molecular weights 9000–31,000 into natural rubber. The diffusion took place into a thin layer of unvulcanized rubber deposited on a strip of vulcanized rubber which could be stretched uniaxially. The diffusion coefficient was observed to decrease substantially with increasing elongation up to a stretch ratio of about 2 and pass through a minimum. In view of the differences in geometry, the relation of these results to ours is not clear, but is probably related to substantial configurational restrictions in the translatory motions of the polymeric penetrants. The average molecular weight between entanglement coupling points in natural rubber is estimated[12] to be about 5700.

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