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AN ANALYSIS OF THE ORIENTATIONAL BIREFRINGENCE OF POLY(METHYL METHACRYLATE) IN TERMS OF THE MOONEY–RIVLIN EQUATION

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Abstract—The orientational birefringence of poly(methyl methacrylate) (PMMA) was analysed using the Mooney–Rivlin equation. It is shown that its dependence on strain can be well described by this equation over more than three decades of time (in seconds). More interestingly, the B_1 term (usually found and ascribed to some temporary affine deformation upon stretching in uncrosslinked polymers) is absent for PMMA within the error of experimental measurements. The B_2 term is shown to be governed by the chain relaxation that takes place during stretching, emphasizing its molecular origin associated with the entanglement network. Also, a comparison of B_1 and B_2 for PMMA and polystyrene (PS) indicates clearly a significant difference between the deformation behaviour of the entanglement network for the two polymers. The B_1 term of PS gives an important contribution to the orientational birefringence, and relaxes with time in a similar way to B_2.

INTRODUCTION

For non-Gaussian rubber-like polymers in uniaxial stretching, the phenomenological Mooney–Rivlin equation is often used to describe the true stress (σ)-strain (λ) and birefringence (Δn)-strain (λ) relations:

$$\sigma = (2C_1 + 2C_2\lambda^{-1})(\lambda^2 - \lambda^{-1}) \qquad (1)$$

and

$$\Delta n = (B_1 + B_2\lambda^{-1})(\lambda^2 - \lambda^{-1}) \qquad (2)$$

where λ is the draw ratio l/l_0, l_0 and l being the sample lengths before and after stretching, respectively. C_1, C_2 and B_1, B_2 are empirical constants independent of λ. Although their molecular origin is still not clear, it is widely recognized that C_1 and B_1 are likely to be related to the chemical crosslink network that undergoes affine deformation upon stretching, while C_2 and B_2 are associated with the entanglement (physical crosslink) network. Indeed, it has been shown that C_2 is extremely small for butadiene oligomer networks in which the entanglements are expected to be absent [1], while for uncrosslinked, entangled polymers such as 1,2-polybutadiene [2] and polystyrene (PS) [3], C_2 and B_2 are greater than C_1 and B_1, respectively, indicating the important entanglement contribution to the stress or birefringence. Moreover, a recent study [4] used a series of poly(ester-urethane) block copolymers with various numbers of physical and chemical crosslinks, and showed that the C_2 term is governed by the non-permanent physical crosslinks in these polymers. Therefore, analysing the stress or birefringence development in uniaxial stretching in terms of the Mooney–Rivlin equation may yield useful informations on the behaviour and importance of the entanglement network.

In this paper, we present an analysis of the birefringence obtained in uniaxially stretched poly(methyl methacrylate) (PMMA) using equation (2). By determining B_1 and B_2, the purpose is to obtain some insight into the entanglement behaviour of this polymer. On the other hand, it is of interest to compare the results with those reported for other uncrosslinked polymers, in particular for PS because possible differences in entanglement network between these two polymers have been revealed by orientation studies [5] and mechanical relaxation measurements [6]. Further information is needed to confirm this difference.

EXPERIMENTAL PROCEDURES

The birefringence measurements for uniaxially stretched PMMA were initially performed to compare the orientation results obtained by using i.r. dichroism [7]. The PMMA sample was a commercial product supplied by CdF-chimie with the following characteristics: $\bar{M}_n = 107{,}000$ g/mol, $\bar{M}_w/\bar{M}_n = 1.7$, $T_g = 122°$.

Thin polymer films of about 50 μm were prepared by casting a 7% chloroform solution on a glass plate. The films were dried under vacuum at 80° for 2 hr and then at 130° for 24 hr to remove solvent. Stretching of the films (40 mm in length and 20 mm in width) was carried out by using a stretching machine capable of operating at constant strain rates and well controlled temperatures (stability ≈ 0.05°). Three strain rates ($\dot{\epsilon} = 0.008$ sec^{-1}, 0.026 sec^{-1}, 0.115 sec^{-1}) and five temperatures above T_g, from 131.5 to 150°, were used to obtain samples with different draw ratio λ. Following stretching, the samples were rapidly quenched to room temperature in order to freeze the birefringence resulting from chain orientation.

Birefringence was measured on stretched samples at room temperature. A birefringence modulator [8] was used at a wavelength of 0.59 μm. The thickness of each film was measured by using a Modular 2520/D comparator and averaged along the specimen.

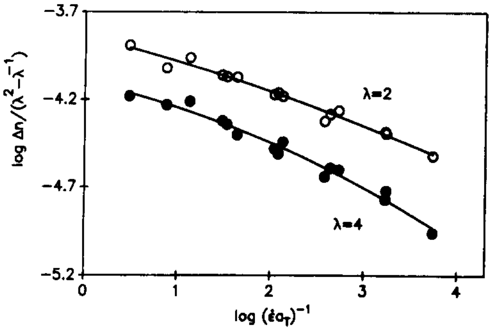

Fig. 1. $\Delta n/(\lambda^2 - \lambda^{-1})$ plotted logarithmically against time $(\dot{\epsilon}a_T)^{-1}$ in sec, reduced to 135°.

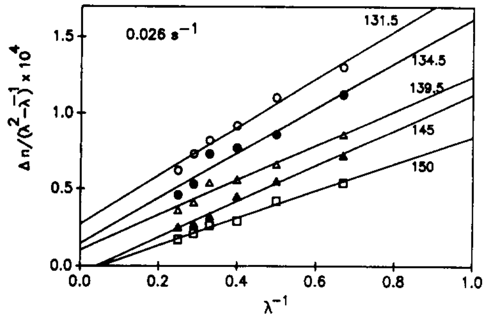

Fig. 3. Plot of $\Delta n/(\lambda^2 - \lambda^{-1})$ against λ^{-1} at strain rate of $0.026\,\sec^{-1}$ for various temperatures (°C) as indicated.

RESULTS

First of all, it should be mentioned that, similar to the orientation behaviour determined from i.r. dichroism [7], the results of the birefringence measurements show clear effects of stretching temperature and rate. The birefringence decreases with increasing temperature or decreasing strain rate. This result is due to the orientation relaxation that takes place during stretching before the sample is frozen and that effect is favoured at higher temperatures or lower strain rates.

The birefringence values obtained at five temperatures and three strain rates were used to determine the master relaxation curve. By analogy to the relaxation of the apparent Young's modulus defined as $3\sigma/(\lambda^2 - \lambda^{-1})$, the birefringence relaxation is obtained by plotting logarithmically $\Delta n/(\lambda^2 - \lambda^{-1})$ against $(\dot{\epsilon}a_T)^{-1}$ in seconds. The master curves reduced to 135° for $\lambda = 2$ and 4 are given in Fig. 1 with the shift factors obtained from the WLF equation [9]: $\log a_T = -11.9(T - 135)/[94 + (T - 135)]$. The $\Delta n/(\lambda^2 - \lambda^{-1})$ quantity decreases as the relaxation time increases over more than three decades of time, and, as can be expected for these large deformations, it is strain-dependent.

The Mooney–Rivlin plots, i.e. $\Delta n/(\lambda^2 - \lambda^{-1})$ vs λ^{-1}, are given in Figs 2–4. In all cases of stretching temperature and rate, a straight line is obtained over the whole range of λ (1.5–4). This result indicates clearly that the dependence of the birefringence on λ under the used conditions can be well described by the Mooney–Rivlin equation. Moreover, from the data in Figs 2–4, linear regression results in the intercept that is B_1 and the slope that is B_2 for each plot. The results for all T and $\dot{\epsilon}$ are given in Table 1. Obviously, the B_1 term is extremely small compared to the B_2 term for every $T - \dot{\epsilon}$. This result indicates a dominant contribution of B_2 to the measured birefringence, while the contribution of B_1 is negligible.

In Fig. 5, the B_1 and B_2 values are plotted as a function of $\log(\dot{\epsilon}a_T)^{-1}$ reduced to 135°. It can be seen that B_2 increases continuously with diminishing relaxation time, while B_1 is apparently near zero and only seems to have a slight positive value at short times.

DISCUSSION

From the reported studies on 1,2-polybutadeine [2] and PS [3], it is known that although the B_2 (or C_2) term makes the largest contribution to the birefringence (or stress), the contribution of the B_1 (or C_1) term is, however, important, especially at short times. The appearance of the B_1 and C_1 terms in these polymers having no chemical crosslinks has been tentatively ascribed to a temporary pattern of affine deformation of the entanglement network upon stretching [2], and this effect is more pronounced at short times. Such a consideration might be extended to a general model involving some kind of permanent network due to "tight" entanglements. The measured birefringence or stress is a result of the combination of the contributions from such tight and the other more labile entanglements.

A striking feature for PMMA is revealed in Fig. 5. In contrast to the polymers mentioned above, within

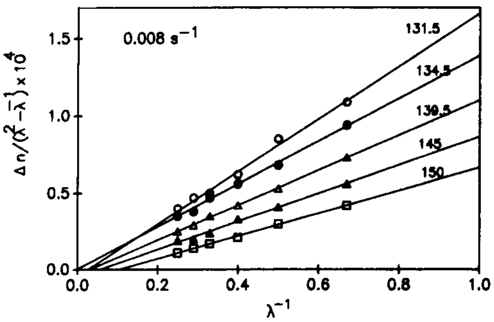

Fig. 2. Plot of $\Delta n/(\lambda^2 - \lambda^{-1})$ against λ^{-1} at strain rate of $0.008\,\sec^{-1}$ for various temperatures (°C) as indicated.

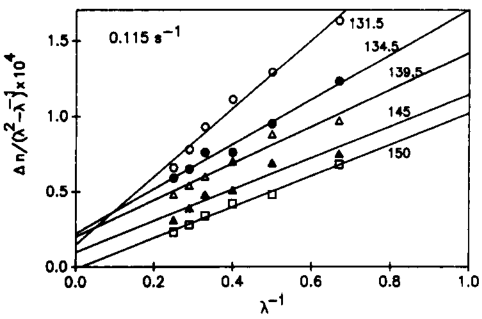

Fig. 4. Plot of $\Delta n/(\lambda^2 - \lambda^{-1})$ against λ^{-1} at strain rate of $0.115\,\sec^{-1}$ for various temperatures (°C) as indicated.

Table 1. Parameters of the Mooney–Rivlin equation for various temperatures and strain rates

T (°C)	$\dot{\epsilon}$ (sec^{-1})	$B_1 \cdot 10^4$	$B_2 \cdot 10^4$
131.5	0.008	−0.04	1.71
	0.026	0.27	1.59
	0.115	0.15	2.26
134.5	0.008	0	1.39
	0.026	0.14	1.48
	0.115	0.22	1.48
139.5	0.008	−0.03	1.14
	0.026	0.10	1.14
	0.115	0.20	1.22
145	0.008	−0.05	0.92
	0.026	−0.05	1.17
	0.115	0.10	1.05
150	0.008	−0.08	0.74
	0.026	−0.05	0.89
	0.115	−0.02	1.03

the error of experimental measurements, B_1 is around zero over the whole time region studied. This effect is particularly evident at relatively long times for which, apparently, even negative B_1 values are obtained (Table 1). This result suggests the absence of the response of some affine deformation upon stretching and a total contribution to the orientational birefringence of an entanglement network that undergoes non-affine deformation. It is interesting to consider the behaviour of PMMA as a special case where there is no contribution from some kind of permanent network (either chemically crosslinked or physically entangled), and the dependence of the birefringence on strain can be described with B_2 alone. The Mooney–Rivlin equation reads:

$$\Delta n = B_2(\lambda - \lambda^{-2}). \quad (3)$$

From the results in Figs 2–5, it is clear that the dependence of B_2 on temperature and strain rate is simply a reflection of its depencence on chain relaxation; B_2 is governed by the amount of the chain relaxation occurring during stretching. As chain relaxation is mostly associated with an entanglement network compared to a crosslinked network, this result is consistent with the assessment that B_2 characterizes the effects of chain entanglement on the birefringence upon stretching. It is worthwhile to note that, in the case of 1,2-polybutadiene, the relaxation of B_2 is observed at relatively long times [2].

It is of interest to compare the entanglement behaviour of PMMA and PS, two important amorphous polymers. An i.r. dichroism analysis [5] showed a higher chain orientation of PMMA compared to PS when they are stretched uniaxially above T_g with the same strain rate and at the same normalized temperature T such that $T - T_g$ is constant. It has been pointed out that this difference in orientation could be attributed to different entanglement networks in these two polymers. A higher entanglement density, characterized by a smaller average molecular weight between entanglements, of PMMA compared to PS may result in a greater chain orientation by stretching. But, it is also possible that this is a result of a smaller amount of chain relaxation of PMMA during stretching, caused by more frictional resistance to the chain relaxation. Further studies are needed to clarify these interpretations.

Now, we want to know whether a possible difference in entanglement network between PS and PMMA can be revealed from the Mooney–Rivlin equation analysis. For this purpose, it is important to use the birefringence results obtained under similar experimental conditions. This comparison is made possible by using the orientation functions P_2 of PS in Ref. [10], which are determined from i.r. dichroism for samples stretched at different temperatures above T_g and strain rates. The orientational birefringence of the PS sample used ($\bar{M}_n = 150{,}000$ g/mol, $\bar{M}_w/\bar{M}_n = 1.7$, $T_g = 105°$), can be calculated from $\Delta n = -0.12\, P_2$ where -0.12 is the intrinsic birefringence of PS [10, 11].

Using the same procedure as described above for PMMA, the birefringence of PS can also be well fitted by equation (2), and the B_1 and B_2 values obtained from linear regression of the Mooney–Rivlin plots are plotted as a function of $\log(\dot{\epsilon}a_T)^{-1}$ reduced to 118° ($T_g + 13°$ as for the PMMA curves reduced to 135°), the shift factors being calculated from [10]: $\log a_T = -9.88\ (T - 118)/[65.6 + (T - 118)]$. Comparing the result shown in Fig. 6 with that for PMMA in Fig. 5 over a similar time range, it is clear that the entanglement behaviour of PS differs significantly from that of PMMA. In contrast with B_1 of PMMA that is around zero, the B_1 term of PS gives an important contribution with a B_2/B_1 ratio of about two over the entire time range. Apparently, this result suggests an affine deformation to some extent in PS upon stretching, being caused by some kind of tight entanglements which do not exist in PMMA. Interestingly, B_1 of PS relaxes in a similar way to that of its B_2 with increasing time. This result seems to

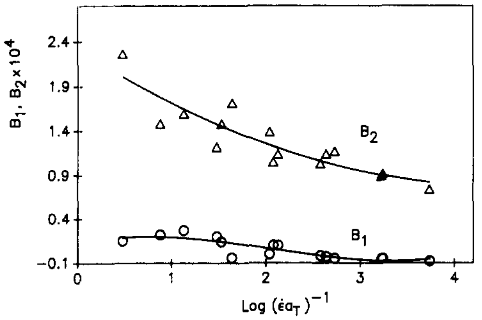

Fig. 5. B_1 and B_2 of PMMA plotted against logarithmic time $(\dot{\epsilon}a_T)^{-1}$ in seconds reduced to 135° ($T_g + 13°$).

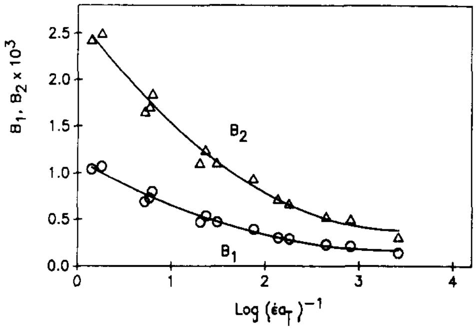

Fig. 6. B_1 and B_2 of PS plotted against logarithmic time $(\dot{\epsilon}a_T)^{-1}$ in seconds reduced to 118° ($T_g + 13°$).

indicate that, for uncrosslinked polymers, B_1 is also related to chain relaxation. In other words, the rigidity or efficiency of the entanglements responsible for affine deformation diminishes with relaxation time just like the other more labile entanglements responsible for non-affine deformation.

Qualitatively, this analysis based on the Mooney–Rivlin equation gives useful information confirming the difference between PS and PMMA in the deformation of the entanglement network by stretching. More studies are however needed to know how this difference affects the chain orientation.

CONCLUSIONS

The dependence on strain of the orientational birefringence of PMMA above T_g can be fairly described by the Mooney–Rivlin equation over more than three decades of time (in seconds). The striking feature revealed for this polymer is that the B_1 term, usually found for other uncrosslinked polymers and ascribed to temporary affine deformation, is absent within experimental error. The B_2 term is shown to be governed by the amount of the chain relaxation during stretching, emphasizing its molecular origin associated with an entanglement network.

On the other hand, a difference between PMMA and PS in the deformation behaviour of the entanglement network by stretching is observed by comparing B_1 and B_2 of the polymers. In contrast with PMMA, PS exhibits a significant B_1 contribution to the orientational birefringence. Moreover, B_1 relaxes with time in a similar way to B_2, suggesting that the rigidity or efficiency of the entanglements responsible for the appearance of affine deformation is also affected by the chain relaxation process.

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