SHORT COMMUNICATION

Stress-Optical Coefficient of Poly(ethylene oxide) and Poly(propylene oxide) Networks. Measurements

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It has become known recently that the stress-optical coefficients of polymer networks which are swollen by optically and geometrically isotropic solvents are found to take minimum values.[1] These results have been obtained for polyethylene,[2,3] *cis*- and *trans*-1,4-polyisoprene, and *cis*- and *trans*-1,4-polybutadiene.[4-8] In this paper we attempt to treat experimentally poly(ethylene oxide), or PEO and poly(propylene oxide), or PPO which contain ether groups in the main chain.

A PEO raw material of viscosity-average molecular weight $M_v \simeq 10^6$ was obtained from the Seitetsu Chemical Company. The PEO sheets were crosslinked at room temperature by irradiating with γ-rays. The radiation doses were varied between about 30 and 50 Mrads. The PPO homopolymer and copolymer with allyl glycidyl ether (3.3 mol%) of $M_v \simeq 1.7 \times 10^6$, and 1.8×10^6, respectively, were supplied by the Tokuyama Soda Company. We preferred to use the crosslinked sheets of PPO copolymer because only a very weak crosslinking was achieved for the homopolymer. The PPO blocks were crosslinked by dicumyl peroxide (2 wt%) and sulfur (1 wt%) with a press temperature 150°C for 30 min. The sample thickness was 1 mm through all measurements. We tried to estimate the linkage imperfections for PPO with the ozonized cleavage method explored by Price, *et al.*[9] The linkage irregularities were determined with a Hitachi K-53 gas chromatography using a 2-m column length packed with 20-% PEG 6000 at 160°C, and a helium flow of 50 ml/min. The results obtained are: head-to-tail

units (I) 83%, tail-to-tail units (II) 8%, and head-to-head units (III) 9% for the homopolymer, while I is 80%, and II and III are 10% for the copolymer. The results of the two types of samples are similar and in good agreement with that of Price, *et al.*,[9] for polymers from the $AlEt_3$—H_2O catalyst system. For the PPO sample with high linkage regularity or high crystallinity it was difficult to obtain a good crosslinking condition. Therefore, only limited stress-optical measurements were carried out for the various samples of PPO.

The stress-optical coefficient of Gaussian networks, C, is given by

$$C = \frac{\Delta n}{\lambda V_r^{2/3} f} = \frac{2\pi}{45kT} \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \Delta \Gamma \qquad (1)$$

where Δn is the birefringence, λ is the elongation ratio, V_r is the volume fraction of polymer, f is the stress referred to the unswollen, unstretched cross section, $\bar{n}$ is the mean refractive index of the sample, k is Boltzmann's constant, T is the absolute temperature, and $\Delta \Gamma$ is the stress-optical anisotropy of a Kuhn statistical segment. The measurements of swollen sheets were limited to only about a 10—15% elongation ratio as the sheets were quite weak.

The values of $\Delta \Gamma$ for PEO are given in Table I. The solvent choices are based on the theta solvent—temperature system found by Bailey and Callard[10] for aqueous salt solutions of No. 1—2, and by Beech and Booth[11] for methyl isobutyl ketone solution of No. 3. The choices are somewhat arbitrary for the others. The $\Delta \Gamma$ in the unswollen states are obtained from the

Table I. Average values of $\Delta\Gamma$ for swollen
and unswollen specimens of PEO

No.	Solvent	V_r	Temp, °C	$\bar{n}$	$\Delta\Gamma$, Å³
1	0.45 M K₂SO₄	0.14	35	1.341	1.34
2	0.39 M MgSO₄	0.18	45	1.345	1.43
3	m.i.b.k.[a]	0.15	50	1.401	1.40
4	CCl₄	0.13	40	1.454	1.35
5	Benzene	0.06	30	1.495	1.24
6	p-Xylene	0.15	30	1.490	1.94
7	Dioxane	0.08	30	1.421	1.38
8	H₂O	0.06	30	1.335	1.57
9	——	1.00	70	1.458	1.31±0.18

[a] Methyl isobutyl ketone.

Table II. Average values of $\Delta\Gamma$ for swollen
and unswollen specimens of PPO

No.	Solvent	V_r	Temp, °C	$\bar{n}$	$\Delta\Gamma$, Å³ [a] $\lambda=1.15$ a	$\Delta\Gamma$, Å³ [a] $\lambda=1.15$ b
1	Isooctane	0.33	50	1.396	1.29	—
2	Cyclohexane	0.21	25	1.421	0.82	0.87
3	Cyclohexane	0.15	50	1.414	1.07	—
4	CCl₄	0.12	25	1.458	1.10	1.20
5	Benzene	0.10	25	1.494	1.30	1.46
6	n-Decane	0.38	40	1.420	1.18	—
7	——	1.00	70	1.442	1.93*	1.99*

[a] a, copolymer; b, homopolymer. The values of V_r
and $\bar{n}$ are somewhat different from those of co-
polymer, but they are not shown here, *$\lambda=1.5$.

Figure 1. Optical anisotropy of PPO vs. elonga-
tion ratio. A, unswollen homopolymer; B, un-
swollen copolymer; C, swollen copolymer with
isooctane; D, swollen copolymer with benzene.

mean value of $\lambda=1.15-1.3$ at 70°C in the ap-
proximately rubbery state. It is noted from
Table I that the $\Delta\Gamma$ of swollen and unswollen
states of PEO are shown to take quite similar
values [ca. 1.35 (Å³)] and are remarkably lower
values than those obtained for polyethylene[7]
[ca. 4.0—9.5 (Å³)].

We next turn our attention to PPO. As can
be seen in Figure 1, a peculiar behavior, devia-
tion from the Brewster's Law, is observed for
the copolymer, even in the swollen state with
benzene and isooctane; i.e., the $\Delta\Gamma$ increases
with increasing elongation ratio below $\lambda=1.5$.
For homopolymer in the bulk state deviation
from Brewster's Law could not be recognized
within experimental error. Such phenomena
can not be adequately explained by form effects
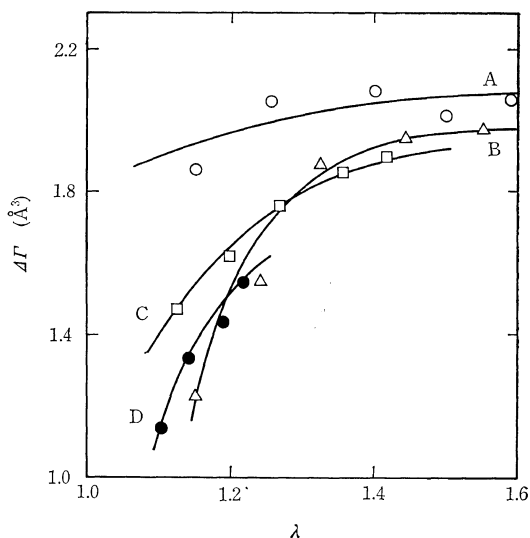or non-Gaussian effects of rubber networks. It

may be pointed out that the experimental error
would mask the intrinsic value in the region of
small birefringence and furthermore reorienta-
tion of the free branches of the allyl glycidyl
ether groups in the copolymer would occur with
increasing elongation. Considering this infor-
mation, we have summarized the results for the
two types of PPO in Table II. The values of
$\Delta\Gamma$ for the swollen state are those at $\lambda=1.15$.
Isooctane, No. 1, is the theta solvent found by
Allen, et al.[12] The saturated values at $\lambda=1.5$
are chosen for unswollen samples, because these
values are similar, and the orientation effect of
the side groups may be eliminated. It is noted
that the $\Delta\Gamma$ of PPO has a larger solvent effect
than that of PEO. It is obvious that the intra-
molecular interaction is larger for the side groups
of PPO than for PEO. We wanted to estimate
the intrinsic value of $\Delta\Gamma$ for PPO, but the
value obtained by the previous technique[5,6]
seems somewhat dubious. One possible reason
is that the $\Delta\Gamma$'s obtained with isotropic solvents
are 0.87 in cyclohexane and 1.46 (Å³) in benzene
for the homopolymer at 25°C. The discrepancy
seems to go much beyond experimental error.
Another aspect is disclosed by Hirano, et al.,[13]
in that the sign of optical rotation for optically

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active PPO is inverted in the above solvents. It indicates the possibility of a conformational change in an isolated chain surrounded with isotropic solvent media, although there is a divergent opinion.[14] The samples employed contain different linkages and stereoirregularities and these effects on the intrinsic value can not be estimated without the aid of theoretical calculations. In any event, the intrinsic value of $\Delta\Gamma$ seems to be obtainable from measurements in the bulk state for PEO, while care must be taken for PPO even in the swollen state in an isotropic solvent.

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