Reports of the Academy of Sciences of the USSR

1963

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1963. Volume 153, No. 5

PHYSICS

E. V. FRISMAN, A. K. DADIVANYAN, G. A. DYUZHEV

ON THE QUESTION OF DETERMINING THE OPTICAL ANISOTROPY OF MACROMOLECULES

(Presented by Academician A. N. Terenin on 4 VII 1963)

It is known that the optical anisotropy of a segment $(\alpha_1 - \alpha_2)$ gives essential information about the structure and flexibility of a macromolecule. In a first approximation it may be assumed that

$$\alpha_1 - \alpha_2 = (a_{\|} - a_{\perp})S,$$

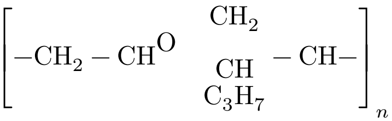
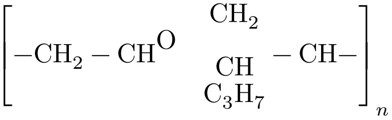
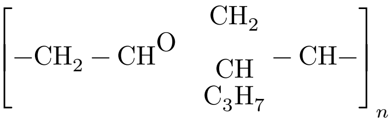
where $(a_{\|} - a_{\perp})$ is the difference in polarizabilities of the monomer unit, and S is the number of monomers in the segment.

The quantity $(\alpha_1 - \alpha_2)$ can be determined from data on the study of dynamic birefringence and the viscosity of polymer solutions (^{1,2}). Until recently it was considered that $(\alpha_1 - \alpha_2)$ does not depend on the properties of the solvent used. However, in the study of molecules of polyvinyl acetate (PVA) an influence of the solvent on the magnitude and sign of the measured segmental anisotropy was found ($^{3-5}$).

Analysis of the experimental data led to the conclusion (^{5}) that the observed phenomenon cannot be associated with a change in the magnitude of the optical segment S. It remained to assume that different values of $(\alpha_1 - \alpha_2)$ are due to the dependence of $(a_{\|} - a_{\perp})$ on the solvent. Calculations carried out according to the valence-optical scheme showed that all experimental values of $(a_{\|} - a_{\perp})$, obtained at $S = 8$ (^{6}), can be explained by assigning to the side group of the PVA molecule a planar trans-configuration with different hindrance to rotation about the C–O bond. From the results of further investigations presented in Table 1, it follows that the state–

Table 1

Measured segmental anisotropy of macromolecules in different solvents

Sample	Solvent	n_s^D	$(\alpha_1-\alpha_2)\cdot 10^{25}$, cm^3	Structural formula
PKhP	Tetrachloroethylene	1.507	50	$[-CH_2-C(Cl)=CH-CH_2-]_n$
PKhP	Toluene	1.497	73	$[-CH_2-C(Cl)=CH-CH_2-]_n$
PKhP	Chlorobenzene	1.525	73	$[-CH_2-C(Cl)=CH-CH_2-]_n$
PE	Decalin	1.476	30	$[-CH_2-CH_2-]_n$
PE	Xylene	1.496	60	$[-CH_2-CH_2-]_n$
PVB-l	Chloroform	1.449	81	 $\left[-CH_2-CH^{O}\begin{matrix}CH_2\\ CH\\ C_3H_7\end{matrix}-CH-\right]_n$
PVB-l	Toluene 79% + phenol 21%	1.497	173	 $\left[-CH_2-CH^{O}\begin{matrix}CH_2\\ CH\\ C_3H_7\end{matrix}-CH-\right]_n$
PVB-l		1.541		 $\left[-CH_2-CH^{O}\begin{matrix}CH_2\\ CH\\ C_3H_7\end{matrix}-CH-\right]_n$
PVP	Chloroform	1.449	−40	$[-CH_2-CH(OCOC_2H_5)-]_n$
PVP	Carbon tetrachloride	1.463	−31	$[-CH_2-CH(OCOC_2H_5)-]_n$
PVP	Benzene	1.501	−4.4	$[-CH_2-CH(OCOC_2H_5)-]_n$
PVP	Toluene	1.497	+1.3	$[-CH_2-CH(OCOC_2H_5)-]_n$
PVB-t	Chloroform	1.449	−48	$[-CH_2-CH(OCOC_3H_7)-]_n$

Sample	Solvent	n_s^D	$(\alpha_1-\alpha_2)\cdot 10^{25}$, cm^3	Structural formula
PVB-t	Carbon tetrachloride	1.463	−36	$[-CH_2-CH(OCOC_3H_7)-]_n$
PVB-t	Benzene	1.501	−8	$[-CH_2-CH(OCOC_3H_7)-]_n$

viewpoint could explain the experimental data obtained for polyvinyl butyrate (PVB-t) and polyvinyl propionate (PVP). But the substantial dependence of $(\alpha_1-\alpha_2)$ on the solvent, observed for molecules of polychloroprene (PCP), polyethylene (PE) [7], and polyvinyl butyral (PVB-l), remains unclear. Indeed, rotation of side groups in PVC and PE molecules cannot noticeably change $(\alpha_\parallel-\alpha_\perp)$. In the PVB-l molecule, however, the side groups are rather rigidly connected with the chain of principal valences, which does not allow one to ascribe any significant mobility to them.

Table 2

Optical anisotropy introduced by the solvent

Sample	Solvent	$(\alpha_1-\alpha_2)\cdot 10^{25}$, cm^3	$(\alpha_1-\alpha_2)_s\cdot 10^{25}$, cm^3	$\delta\cdot 10^{25}$, cm^3	$\frac{(\alpha_1-\alpha_2)_s}{\delta}$
PVA	Chlorobenzene	+14	30	74.0	0.40
PVA	Toluene	+10	26	74.3	0.35
PVA	Benzene	+4	20	63.8	0.32
PVA	Xylene	+2	18	77.8	0.23
PVA	Carbon tetrachloride	−16	0	0	
PVA	Chloroform	−24	8	28.2	0.30
PVA	Cyclohexanone	−23	7	21.8	0.32
PVA	Dichloroethane	−36	20	45.0	0.44
PVP	Chloroform	−40	9	28.2	0.32
PVP	Carbon tetrachloride	−31	0	0	
PVP	Benzene	−4.4	26.6	63.8	0.41
PVP	Toluene	+1.3	32	74.3	0.43
PVB-t	Chloroform	−48	12	28.2	0.32
PVB-t	Carbon tetrachloride	−36	0	0	
PVB-t	Benzene	−8	28	63.8	0.44

It is noteworthy that the use of aromatic solvents leads to large values of the measured segmental anisotropy. This makes it possible to suppose that the different values of $(\alpha_1 - \alpha_2)$ obtained in different solvents are due not to a rearrangement of the macromolecules, but to the properties of the surrounding medium.

We believe that, near the monomer units of the chain, an ordered arrangement of solvent molecules (short-range order) arises; these molecules contribute to the measured segmental anisotropy. In this case, the quantity $(\alpha_1 - \alpha_2)$ determined experimentally must contain two terms:

$$\alpha_1 - \alpha_2 = (\alpha_1 - \alpha_2)_k + (\alpha_1 - \alpha_2)_s,$$

where $(\alpha_1 - \alpha_2)_k$ is the true optical anisotropy of the segment; $(\alpha_1 - \alpha_2)_s$ is the anisotropy introduced by solvent molecules oriented relative to the chain units*. The quantity $(\alpha_1 - \alpha_2)_s$ must be determined by the difference of the polarizabilities of the solvent molecules, the character of their orientation, and the number of oriented molecules per segment, i.e., by the flexibility of the chain. Thus, the quantity $(\alpha_1 - \alpha_2)_k$ can be directly determined from experiment only when an isotropic solvent is used. One may assume that the value of $(\alpha_1 - \alpha_2)$ obtained for molecules of PVA, PVP, and PVB-t in CCl_4 characterizes the segmental anisotropy of these chains. Then the difference between this quantity and the values of $(\alpha_1 - \alpha_2)$ obtained for the macromolecules under consideration in other solvents gives the excess anisotropy $(\alpha_1 - \alpha_2)_s$, caused by the presence of short-range order (Table 2). If the data from studies of the Kerr effect in gases are then used, one can calculate the optical anisotropy of the polarizability of the solvent molecules:

$$\delta^2 = \frac{1}{2}\left[(\alpha_1 - \alpha_2)^2 + (\alpha_2 + \alpha_3)^2 + (\alpha_3 - \alpha_1)^2\right].$$

The ratio $(\alpha_1 - \alpha_2)_{s/\delta}$, given in Table 2, remains approximately constant for all solvents, which, as it seems to us, speaks in favor of the point of view developed here. Unfortunately, we were unable to carry out a similar analysis for the other macromolecules studied here, since it was not possible to select an isotropic solvent that would make it possible to obtain a system not possessing a shape effect (8).

As has already been indicated, the quantity $(\alpha_1 - \alpha_2)_s$ should depend on the flexibility of the chain. The enormous difference in the values of $(\alpha_1 - \alpha_2)$ obtained for the PV molecule in different solvents is apparently due to the great rigidity of the polymer chain (the large value of the optical segment).

---

* We note that the anisotropy introduced by a solvent oriented by a laminar flow is always taken into account.

The fact that until recently no mention was made of the influence of order on the measured segmental anisotropy is due, above all, to the absence of systematic measurements of $(\alpha_1 - \alpha_2)$ in different solvents. Moreover, when very anisotropic macromolecules are studied in one class of solvents (9) (aromatic or nonaromatic), the difference in the values of $(\alpha_1 - \alpha_2)$ is small and may lie within the limits of experimental error.

The data presented show that the role of short-range order in the measured value of $(\alpha_1 - \alpha_2)$ is especially large in the study of macromolecules possessing small anisotropy or considerable rigidity.

In conclusion, we note that the large experimental value of the difference in polarizabilities of the monomer unit, obtained for polyisobutylene in benzene (10), which is not compatible with that expected from the valence-optical scheme, is to a considerable extent due to the nature of the solvent used.

Physical Institute,
Leningrad State University
named after A. A. Zhdanov

Received
30 VI 1963

REFERENCES

1. W. Kuhn, H. Kuhn, *Helv. Chim. Acta*, **26**, 1395 (1943).
2. A. P. Peterlin, *J. Polym. Sci.*, **12**, 45 (1954).
3. E. V. Frisman, V. Ya. Andreichenko, *Vysokomolek. soed.*, **4**, 1559 (1962).
4. E. V. Frisman, An Bao Chzhu, *Vysokomolek. soed.*, **4**, 1564 (1962).
5. E. V. Frisman, G. A. Dozhev, A. K. Dadivanyan, Abstracts of the VI Conference on Liquid State, Kiev, 1963.
6. A. Schuitz, *J. Am. Chem. Soc.*, **76**, 3422 (1954).
7. T. I. Garmonova, *Vestn. Leningradsk. univ.*, ser. phys. and chem., No. 22, 72 (1962).
8. V. N. Tsvetkov, E. V. Frisman, *DAN*, **97**, 647 (1954).
9. E. V. Frisman, V. N. Tsvetkov, *J. Polym. Sci.*, **30**, 297 (1958).
10. V. N. Tsvetkov, V. E. Bychkova, S. M. Savvon, I. K. Nekrasov, *Vysokomolek. soed.*, **1**, 1407 (1959).