Structural Changes in Polyethylene Films at Small Deformations

YU. S. LIPATOV, E. G. MOISYA, P. N. LOGVINENKO, and G. YA. MENGERES, *Institute of Macromolecular Chemistry, Academy of Sciences, Ukrainian, SSR, 252160, Kiev, USSR*

Synopsis

Structural changes in PE films at deformation 2–7% under constant load were studied by molecular probe method. It was shown that at these conditions some structural rearrangements take place which involve more than 20% of polymer volume, only 2–3% being transformed in the state of three-dimensional ordering. The most part of ordering observed was connected with two-dimensional ordering in the AC plane of molecular folding, involving tie chains near the crystallites. The effect of relaxation process during deformation on structural rearrangements in PE films was also investigated.

Structural changes in semicrystalline polymers during uniaxial stretching studied by many authors yielded information concerning some general features of the phenomena involved, but in no case so far detailed was a study of structural changes accompanying small deformations reported. Moreover, since deformation processes in this range are reversible, it is usually tacitly assumed that after unloading, the initial structure of a specimen is reversible recovered. However, using the molecular probe (MP) technique in the investigation of structural changes in polymer subjected to various physical actions, we were able to discover distinct signs of structural transformations even at rather small levels of deformation, which stimulated undertaking their detailed investigation.

In this paper, we present some results of investigations of structural changes in films from low-pressure polyethylene (PE). Film thickness was about 100 microns. As before,[1-3] anthracene (A) molecules were used as impurities, their concentration in PE being 10^{-3} g/g. Anthracene was melted with PE at 20° above the polymer melting point in a pressform, the time of melting being about 50 min. Cooling was realized in the pressform by a natural heat transfer in three ways: down to 50°, to room temperature, and to room temperature with following heat treatment at 100° under vacuum during 1 hr. As a result of such preparations, we obtained PE films with more or less ordered initial structure. Relative elongation of specimens during 25–30 days of constant load action ranged from 2% to 7%.

Absorption and/or fluorescence spectra of molecule probes in amorphous

and crystalline regions of a matrix polymer (hereafter referred to as AM and CR impurity spectra, respectively) in our MP method yielded information on the relative content of amorphous and crystalline regions in the initial sample, as well as on the change of this content during various structural actions on polymer. Moreover, change of positions of impurity spectra may be used to estimate density changes in the matrix (that is, corresponding decrease or increase of molecular packing density in this or that phase). Detailed description of the theoretical foundations of the MP method as well as its experimental verification and procedure can be found in the original papers.[1–3]

We have studied structural changes in PE films for two cases, viz., (a) constant load applied to unoriented films, and (b) the same for oriented films (relative elongations amounted to 1000–1300%). Besides, effect of relaxation processes during the deformation process on polymer structure was also investigated.

We have two types of impurity centers of anthracene in PE and correspondingly two impurity spectra (in absorption and in fluorescence). Changes of relative content of amorphous and crystalline regions in the course of structural action were estimated from relative intensities of AM and CR impurity spectra (J_{AM} and J_{CR}, respectively) of anthracene molecules located in corresponding regions of PE. In general, such investigation may be carried out by adsorption spectra as well as by fluorescence spectra of impurity molecules. We can also observe changes in relative intensity of impurity spectra,[1–3] taking into account the value of the ratio $r = J_{AM}/J_{CM}$ for different cases and spectral shifts due to changes in molecular packing density of a matrix around a molecule probe.[3] In both cases, we can clear up the character of changes in polymer structure and evaluate their range, but both these versions of the MP method have their advantages and limitations. Adsorption spectra give directly the number of AM and CR impurity centers in PE and its change in the course of structural action. This allows one to estimate the polymer fraction taking part in structural transformation. However, in many cases only 2–10% of the polymer volume are involved in structural transformation, and therefore the experimental value is comparable with the experimental accuracy (±1%).

Fluorescence spectra give the ratio J_{AM}/J_{CM} which is nonlinear, dependent on the number of AM and CR regions in PE,[3,4] since due to processes of energy migration, the relative intensity of CR spectra increases (energy migration to the lowest energy level in the system takes place, namely, to CR level of A in PE[1–4]). Taking fluorescent spectra, we obtain higher changes of the ratio $r_{fl} = J_{AM}{}^{fl}/J_{CR}{}^{fl}$ of polymer unit volume taking part in structural transformation as compared to the absorption spectra. In the present study, we have used both methods of investigation: we have investigated absorption and fluorescent spectra of A in PE. As a result of variation in the thermal conditions of sample preparation, the values of ratio r for initial samples PE with A ranged from 3.2 and 1.4 (see Table I).

It was established that J_{AM}/J_{CM} decreases (i.e., the amorphous phase content decreases) when the time of action of constant load increases, the specimen structure becoming more and more ordered. The dependence of the ratio r on the loading time T in all cases studied was approximately linear. It was found that the ratio r changes more the greater its value for the initial

TABLE I

Values of the Ratio J_{AM}/J_{CR} for Impurity Spectra of Anthracene in Various Initial PE Samples and Corresponding Values of Term a in the Linear Dependence of this Ratio on the Time of a Constant Load Action T_{load}

	Unoriented PE films										Oriented films			Unoriented films with anthracene and quinone			
	$\sigma = 2$ kg/mm²							$\sigma = 5$ kg/mm²									
Ratio J_{AM}/J_{CR} for initial samples	3.2	3.2	3.0	1.8	1.7	1.5	1.4	1.6	1.3	3.0	2.1	1.8	1.8	3.2	3.1	1.7	1.7
Term $a \times 10^2$ in the linear dependence	9.0	7.5	8.0	4.0	3.5	3.2	3.2	15.0	15.0	9.0	3.5	3.5	3.6	8.0	8.0	3.5	3.4

sample, i.e., the smaller the degree of ordering of the structure. Presenting the dependence of the ratio r on T as a function $r = f(T) = ax + b$, we have found (see Table I) that if initially we have $r = 3$, term a in the above equation ranged from -0.08 to -0.01; for initial r $= 1.5$, we have $a = -0.03$. This pattern holds both for initial undeformed PE films as well as for ultimately stretched (i.e., irreversibly oriented by more than 1000%) samples. In those cases when PE was stretched by higher constant load, $\sigma = 5$ kg/mm^2, structural rearrangement in the sample proceeded at a higher rate (term a was of the order -0.15, see Table I).

The effect of relaxation processes during deformation on structural rearrangements in PE films was also investigated. First, it was established that lowering of the ratio r has been continued for some time even after unloading of the sample; and second, immersion of stretched sample into xylene results in the increased drop r (this effect was absent for control unstretched sample of PE with A immersed in xylene).

Dynamics of the relaxation process was studied in detail in the series of experiments involving consecutive loading and relaxation of samples (see curves 1 to 3 in Fig. 1). It was found that when a sample was allowed to relax after the prolonged action of constant load (for example, after nine days), the effect of relaxation on the structure was insignificant (full and dotted lines in curve 1, Fig. 1). However, the effect of relaxation processes in structural rearrangements turned out to become the more evident the earlier the stage of sample deformation (cf. dotted portion of curves 1 to 3, Fig. 1). In those
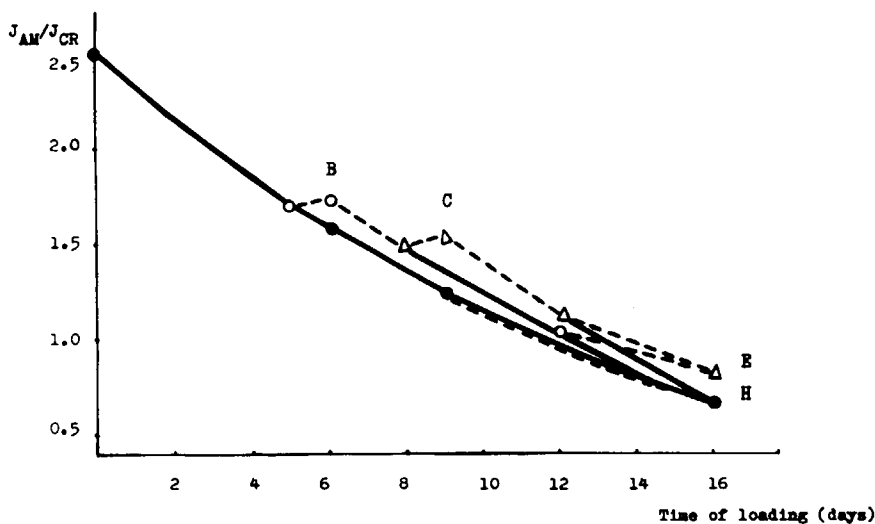

Fig. 1. Change of relative intensity of impurity AM and CR fluorescence spectra of anthracene in polyethylene during reversible stretching and relaxation: (1) change of J_{AM}/J_{CR} with increased time of a constant load action; dotted portion on the curve corresponds to the samples released from the clamps after nine days of stretching and relaxing; (2) curve for samples loaded during five days, relaxed for one day, and subsequently subjected to the same loading; (3) same as (2), but relaxation allowed after nine days. Impurity anthracene spectra were measured using spectrometer ISP-51 at 77°K, anthracene fluorescence exited with the aid of a DRS-500 lamp with light filter $l_{max} = 365$ nm.

samples which relaxed after definite stretching stage, final values of the ratio r (that is, final degree of order of macromolecules) may be different (compare points D and E in Fig. 1).

The results given above describe qualitatively some peculiarities of PE structure transformation under constant loading. To find out the value of polymer fraction taking part in structural ordering, we have investigated changes in molecular probe absorption spectra. From these spectra, we have estimated that nearly 40% of amorphous regions are involved in structural transformations (15–20% of total polymer volume). The shifts of the AM spectra to the long-wave region was also observed, which shows the average density of amorphous regions to be increased by 3%.

Some additional information on structural changes in samples under investigation was provided by complementary x-ray in IR absorption spectra data. We have estimated that initial crystallinity (67%) after 16-day loading increases by 2–3%. Crystallite dimensions also increase from 115 Å to 130 Å.

In the structural studies reported above, rather small loads were used (2 kg/mm^2, see above). Appearance of macroradicals in polymer under load as well as sample rupture occur according to Moisya et al.[5] at higher loadings, say, 35–40 kg/mm^2. Nevertheless, the eliminate the possibility of radical processes and corresponding contribution in spectra from chemical compounds of A so formed to the change of the ratio r,[6,7] we have carried out a series of control experiments as described below. All other conditions being unchanged, we introduced quinone into PE samples with A, quinone concentration being 10^{-3} g/g and ratio to anthracene concentration being 1:1. It was found that quinone, which is a well-known inhibitor of radical processes, did not affect the pattern of observed changes of J_{AM}/J_{CR}. Moreover, it turned out that in this case also, as in the case of PE with A, variation of the ratio r depends only on the value of the latter for initial sample. In other words, the term a in the linear dependence referred to above is about -0.08 for samples with initial ratio $r = 3$ and -0.03 for samples with $r = 1.5$ (see Table I).

Comparison of the experimental results allows the conclusion to be drawn that more than 20% of polymer volume takes part in structural rearrangements, but only 2–3% are transformed in the state of three-dimensional ordering. The most part of ordering observed must in such a way be connected with two-dimensional ordering, probably in the AC plane of molecular folding.

It is also possible to connect these changes with tie chains near the crystallites. We believe this is the reason why this phenomenon was not discovered by traditional methods earlier. Only Natov et al.[7] observed some structural changes in PE during long mechanical action. The molecular probe method is highly sensitive and allows one not only to discover the structural rearrangements but to observe their character and changes.

References

1. E. G. Moisya and Yu. P. Egorov, *Zh. Prikl. Spectr.*, **1**, 363 (1964).
2. Yu. P. Egorov and E. G. Moisya, *J. Polym. Sci. C*, **16**, 2031 (1967).
3. Yu. P. Egorov, E. G. Moisya, and I. A. Ar'ev, *Teor. Exper. Khim.*, **3**, 772 (1967).

4. S. N. Zhurkov, V. A. Zakrevskii, V. E. Korsukov, and V. S. Kuksenko, *Fiz. Tv. Tela,* **13,** 2004 (1971).

5. E. G. Moisya, Yu. S. Lipatov, P. N. Logvinenko, and G. M. Semenovich, *Tepr. Exper. Khim.,* **10,** 277 (1974).

6. L. S. Bogdan and A. A. Kachan, *Vysocomol. Soedin.,* **A16,** (1974).

7. M. A. Natov, S. V. Vasileva and V. S. Kabaivanov. Vysocomol. Soedin., **A11,** 1291 (1969).