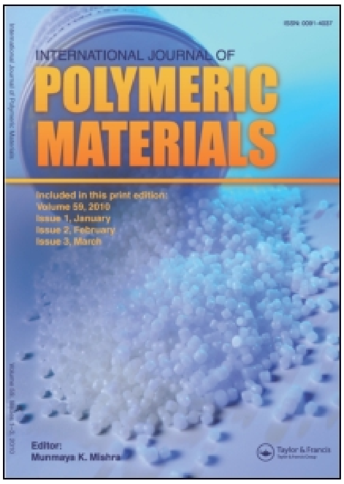

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# Kinetics of Radical Decay and Molecular Dynamics in Oriented High Modulus Polyethylene

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The kinetics of decay of macroradicals in irradiated ultradrawn (draw ratio 200) high modulus polyethylene, single crystal mats of polyethylene and polyethylene with extended chain crystals was studied comparatively by the ESR technique. The results were analyzed from the viewpoint of correlations between the microstructure and temperature-dependent chain dynamics of the polymers. The actual absence of appreciable radical decay in the temperature range 200–300 K and a remarkable stability of considerable fraction of initial radicals at higher temperatures in high modulus sample were explained by extremely restricted motion of the fragments of unfolded tie molecules in trans-conformations predominating in the amorphous region of this polymer. In addition, direct evidences for drastic conformational changes in amorphous regions of polyethylene as a result of ultradrawing obtained by IR-spectroscopy are reported.

KEY WORDS High modulus polyethylene, macroradicals, decay, electron spin resonance, infrared spectroscopy, molecular motion.

## INTRODUCTION

Kinetics of the reactions of active species in solid polymers is determined principally by the local and cooperative molecular motion in the polymer matrix. The correlation between the radical decay in irradiated samples and the relaxation spectra of the polyolefines was observed in extensive experimental studies pioneered more than 25 years ago[1,2] and reviewed by several authors.[3–5] In these studies the radiation-induced radicals may be regarded as inner "labels" which allow to follow the chain motion specificity.

Various factors are generally believed to play an important role in the radical decay kinetics in semicrystalline polymers (e.g. in PE), these are: the degree of crystallinity, crystal size, crystal and interface defects, chain dynamics in the amorphous region. According to Reference 6 the uniaxial orientational deformation of single crystal mats of PE (up to draw ratio DR = 200) has only an insignificant effect on the X-ray degree of crystallinity of the sample, causing, however, dramatic structural changes in the amorphous region. The study of radical recombination in highly oriented samples appears to be effective for obtaining information concerning the specific features of molecular dynamics of extended chains in the amorphous region.

We report here the results of comparative studies of radical decay kinetics in PE single crystal mats, ultradrawn high modulus PE and PE with extended chain crystals (ECC PE). In addition, we present some results from the analysis of conformational changes which occur in ultradrawn samples as revealed by IR-spectroscopy. The aim of the present work is:

(i) to study the effects of ultra-orientation on radical decay reactions,

(ii) to establish the correlation between the microstructure of high modulus PE and chain dynamics,

(iii) to investigate principal thermal stability of the macroradicals in irradiated high modulus PE.

## EXPERIMENTAL

### Materials and sample preparation

Single crystal PE mats were prepared by crystallization from dilute (0.1–0.3 wt %) solutions of high density linear PE ($M_w = 10^6$, degree of branching 0.05 $CH_3$ per 100 C) in xylene. Highly oriented high modulus PE samples (DR = 200, $E = 150$ GPa) were obtained by two-stage drawing of the mats at 393 K. ECC PE (degree of crystallinity 95–98%) was prepared from the drawn (DR = 15) high density linear PE by crystallization under high pressure as described in Reference 7.

### Irradiation and spectral measurements

The samples were irradiated with $^{60}$Co $\gamma$-rays under vacuum ($\sim 10^{-3}$ Torr) at 77 K up to comparatively small "diagnostic" dose (10 kGy). In some experiments high modulus PE samples were irradiated at room temperature (295 K) up to the total dose *ca* 100 kGy.

The ESR spectra were measured with a standard X-band spectrometer with HF-modulation 100 kHz. For the samples irradiated at 77 K all spectra were recorded at 110 K after annealing the sample for 10 min at required temperature. For the samples of high modulus PE irradiated at room temperature the spectra were recorded at 295 K. The total concentration of paramagnetic species (mainly alkyl radicals) was calculated by double integration of the experimental first-derivative spectra.

The IR-spectra were measured with a FTIR Spectrometer Perkin–Elmer 1710. The spectra of oriented high modulus samples were measured in polarized light using Ge-polarizer.

## RESULTS AND DISCUSSION

### Structural aspects

As was shown by X-ray analysis,[6] orientational deformation of the samples of PE mats is not accompanied by essential changes in the volume crystallinity and structure of crystalline regions (after formation of fibrillar structure at small deformations). The fraction of crystal defects characterized by the paracrystallinity parameter[6] remains practically unchanged throughout the drawing of the sample from DR = 20 to 200. On the other hand, the fraction of unfolded tie molecules in the amorphous regions calculated from X-ray data[6] increases dramatically in the course of drawing (from 13% at DR = 15 to 73% at DR = 200).

The present study reports direct IR-spectroscopic evidences for striking conformational changes in highly oriented samples. The quantitative data which reflect the changes in the

TABLE I
Conformational changes in PE resulting from ultradrawing of single crystal mats as revealed by changes of the ratios of characteristic IR-bands

| Sample | $D_{2016}/D_{1368}$ | $D_{2016}/D_{1352}$ | $D_{2016}/D_{1306}$ | $D_{2016}/D_{1896}$ |
|---|---|---|---|---|
| 1 (single crystal mats) | 0.5 | 0.8 | 1.4 | 1.8 |
| 2 (oriented high modulus PE) | 2.4 | 4.1 | 16.0 | 1.4 |

$D_{\bar{\nu}}$ is an optical density of a band with maximum positioned at wave number $\bar{\nu}$. See the text for identification of the bands.

IR-spectrum as a result of ultradrawing of single crystal mats are given in Table I. According to Reference 8 the bands with maxima positioned at 1368, 1352, and 1306 $\text{cm}^{-1}$ are attributed to the conformers GTTG′, GG, and GTG′, respectively. All these *gauche*-containing conformers are assigned mainly to the folded tie molecules and irregular long loops localized in amorphous regions of the polymer.[9] On the other hand, the band with maximum positioned at 2016 $\text{cm}^{-1}$ is associated with $T_m$-type conformers ($m = 4$–$7$) in the chains localized both in crystalline and in amorphous regions, and the band with maximum at 1896 $\text{cm}^{-1}$—with the *trans*-sequences of methylene groups ($m > 7$) in crystalline regions.[10] Thus the observed changes (five-fold increase of the ratios $D_{2016}/D_{1368}$ and $D_{2016}/D_{1352}$) provide clear evidence for effective GTTG′ → TT and GG → TT transitions in the chains in amorphous regions due to ultradrawing. The obtained results are in good agreement with the X-rays analysis data.[6] The most striking increase of the ratio $D_{2016}/D_{1306}$ should be a subject for a special discussion.

## KINETICS OF RADICAL DECAY AND CHAIN DYNAMICS

It is well known[3,4] that irradiation of any type of PE at 77 K results mainly in the stabilization of interior alkyl-type macroradicals $-CH_2-\dot{C}H-CH_2-$. In unoriented single crystal PE mats these radicals reveal a broad sextet spectrum with a hyperfine splitting of about 33 G, which agrees well with the spectra reported by many other authors.[3,4] In the highly oriented system we observed a characteristic dependence of the spectrum upon orientation of the draw axis toward the magnetic field resulting from remarkable anisotropy of $\alpha$-proton hyperfine coupling.[3] However, in our experiments small pieces of ultradrawn high modulus PE (thickness about 10 $\mu$m, length 8–10 mm) were oriented in the ESR ampoule in an essentially disordered (but not effectively random) manner. This suggests a complicated spectral interpretation. This paper does not present a detailed analysis of qualitative changes in the ESR spectra upon annealing. However, the total spectral width and the general character of the spectra enable a conclusion that alkyl-type macroradicals are predominant paramagnetic species in high modulus PE (as well as in ECC PE) within the studied temperature range.

The stepwise character of the radical decay process is characteristic of kinetics of radical recombination in solid polymers resulting from principal kinetic unequivalency of reacting species which can be analyzed in terms of various energetic and spatial distributions.[11] This type of kinetics is qualitatively characterized by a considerable drop in the reaction rate at a given temperature at rather small conversions in the time range of the order of minutes. The obtained result makes it possible to use the so-called “radical decay curves”

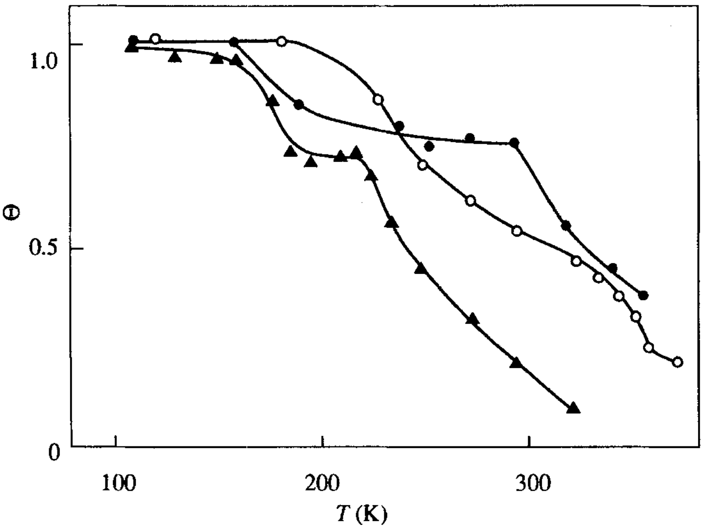

FIGURE 1 The dependence of radical fraction Θ survived after annealing in PE single crystal mats (▲, sample 1), ultradrawn high modulus PE (●, sample 2) and ECC PE (○, sample 3) irradiated by 1 Mrad at 77 K on the annealing temperature. Annealing time is 10 min, registration temperature is 110 K.

to describe the temperature-dependent kinetics of radical decay, since the curves represent the fraction of radicals which survived after annealing the sample for a certain period of time at different temperatures. Analysis of radical decay curves appears to be effective in obtaining semi-quantitative information on chain dynamics. Although the assumption of stepwise kinetics is not entirely valid for the temperatures above glass transition point, this approach is used in a wide temperature range and shows a reasonably good correlation with the data on molecular dynamics obtained by other methods.[3,4]

The radical decay curves for the irradiated samples of PE single crystal mats (sample 1), ultradrawn high modulus PE (sample 2) and ECC PE (sample 3) are presented in Figure 1. Comparison of the radical decay in oriented high modulus PE and ECC PE seems to be of interest from the viewpoint of structural consideration. According to Reference 6 the ECC PE sample has the most perfect crystal (judging from paracrystallinity parameter values) and the chain dynamics in this polymer in the temperature range 100–400 K can be determined principally by non-crystalline regions, whose fraction is very small. Some aspects of radical decay kinetics and chain dynamics in ECC PE were discussed previously.[12] It is to be noted that there are some discrepancies in experimental results concerning the radical decay kinetics in irradiated ECC PE reported by different authors which probably originate from differences in the sample microstructure and the preparation technique. Our data are in a reasonable agreement with those reported in References 13–15.

For convenience we will consider three main temperature regions of the radical decay curves: below 200 K (I), 200–300 K (II), and above 300 K (III).

In temperature region I one can observe some radical decay in samples 1 and 2 at 160–180 K, and practically no decay in sample 3. This decay is probably due to some local process ($\gamma$-relaxation). We conclude that the following reasons account for the fact that this process occurs mainly in the vicinity of crystal defects or at the interphase boundary.

(i) The decay is observed both for single crystal mats (sample 1) and for high modulus

PE (sample 2). The crystal defects in these samples by their nature are almost similar, whereas the structure of amorphous regions differs dramatically (see above).

(ii) The decay is negligible in sample 3 which has a more perfect crystal structure and a larger crystallite size.[6] The most striking feature of the experimental curves in temperature region II is the absence of radical decay in sample 2 in the range of glass transition of PE (220–250 K). This is due to the extremely restricted motion of unfolded tie molecules which are most abundant in the amorphous region of this sample.

Note that rather effective radical decay in this temperature region is observed for sample 3 with only a slight temperature shift (compared to sample 1) in spite of the insignificant fraction of amorphous regions in the sample. In the third temperature region (above 300 K) the radical decay is observed in all the samples and is most effective in single crystal mats (less than 10% of the radicals survive at 320 K). One more temperature region of fast radical decay (340–360 K) seems to be important for ECC PE. In the previous paper we attributed this decay to relaxation of some specific chain fragments (such as short loops) in the intercrystallite region.[12] The radical decay in high modulus PE occurs markedly at the temperatures above 300 K. It is noteworthy, however, that a large fraction of initially produced radicals survives in this sample after annealing at comparatively high temperatures (more than 35% at 353 K). This fraction is actually even greater than in ECC PE sample, which is characterized by extremely high crystallinity. This leads to the conclusion that the observed stability of macroradicals results from high rigidity of the unfolded tie molecules rather than from localization of "persistent" radicals in the crystal regions of the polymer.

Considering the role of molecular dynamics in radical decay processes in PE one must take into account two principal steps of the process: (i) migration of radical site and (ii) recombination of the pair of radicals at adjacent chains yielding a cross-link. The mechanism of radical site transport and the significance of the relevant molecular motions have been the subject of discussion in the literature for a long time.[3–5] Convincing experimental and theoretical evidences for favorable interchain H-atom migration at 100–350 K were presented.[14] The final step, the interchain recombination occurs in the amorphous region[5] and is accompanied by considerable structural reorganization in the nearest environment of the radical pair, which suggests some specific molecular motion. We believe that a sharp increase in the fraction of unfolded tie molecules in an ultradrawn sample has a considerable effect both on radical site migration and on the recombination step. On the one hand, the interchain transport of radical site is facilitated by interchain oscillations which seem to be essentially restricted for taut tie molecules predominating in amorphous regions of the sample. On the other hand, the recombination of two radicals located at adjacent unfolded tie molecules in ideal *trans*-conformations (as well as in an ideal crystal) is hardly likely from the structural and energetic point of view. We conclude that the chain defects both in crystal and in "amorphous" (i.e. characterized by the absence of three-dimensional order)[6] regions must play a major part in radical decay in the ultradrawn high modulus PE.

In order to investigate the principal thermal stability of radiation-induced macroradicals in high modulus PE, which is essential from the viewpoint of possible modification and ageing of the material, we studied the radical decay in the sample irradiated at room temperature up to a high absorbed dose (100 kGy). In this case about 80% of the initially produced paramagnetic species survive after annealing the sample for 30 min at 373 K. In fact, no appreciable decay was observed in the range of annealing temperatures 330–373 K (some radical decay did undoubtedly occur during irradiation). Considerable decrease of radical concentration takes place only after annealing the sample at the temperatures above 390 K. The study of characteristics of these very stable macroradicals (localization, relaxation properties, chemical reactivity toward different agents) appears to be of significant interest. Preliminary results show that the post-irradiation exposure to air has a comparatively small effect on the decay of these radicals at 353 K.

## CONCLUSIONS

The alkyl radical decay in highly oriented high modulus PE is characterized by some peculiar features: the absence of observable decay in the temperature region 200–300 K and a very high thermal stability of the considerable fraction of radicals. We attribute this result to the extremely restricted motion of the chain fragments of unfolded tie molecules predominating in amorphous regions of this sample.

The comparative studies of radical decay in irradiated single crystal mats of PE, ultradrawn high modulus PE and ECC PE suggest that the principal features of radical decay are determined mainly by a specific microstructure and defects in crystal and amorphous regions. It seems to be a good reason for using the radical decay probe technique as a sensitive tool to investigate correlation between the polymer microstructure and the chain dynamics.

## References

1. H. Kashiwabara, *Jpn. J. Appl. Phys.*, **3,** 384 (1964).
2. S. Nara, H. Kashiwabara, and J. Sohma, *J. Polym. Sci.*, **A2,** 929 (1967).
3. M. Dole, *The Radiation Chemistry of Macromolecules,* Ed. M. Dole, (Academic Press, New York 1972), Vol. 1, Chap. 14.
4. V. K. Milinchuk, E. R. Klinshpont, and S. Ya. Pshezhetskii, *Makroradicaly,* (Khimiya, Moscow, 1980).
5. J. Bartoš and J. Tiňo, *Polymer,* **27,** 281 (1986).
6. S. N. Chvalun, E. A. Sinevich, M. B. Konstantinopolyskaya, V. S. Schirets, Yu. A. Zubov, and N. F. Bakeev, *Vysokomol. Soedinen.*, **A30,** 1962 (1988).
7. Yu. A. Zubov, V. I. Selikhova, M. B. Konstantinopolyskaya, F. F. Sukhov, N. A. Slovokhotova, N. F. Bakeev, A. V. Kryukov, and V. A. Sokolskii, *Vysokomol. Soedinen.*, **A14,** 2090 (1972).
8. G. Zerbi, *Pure Appl. Chem.*, **26,** 499 (1971).
9. V. I. Vettegren, V. A. Marikhin, L. P. Myasnikova, A. Popov, and G. Bodor, *Vysokomol. Soedinen.*, **A28,** 914 (1986).
10. S. Krimm, *Adv. Polym. Sci.*, **2,** 51 (1960).
11. A. L. Buchachenko and N. M. Emanuel, *Khimicheskaya Fizika Stareniya i Stabilizatsii Polimerov,* (Nauka, Moscow, 1982).
12. F. F. Sukhov, V. I. Feldman, S. M. Borzov, and N. A. Slovokhotova, *Vysokomol. Soedinen.*, **A30,** 2213 (1988).
13. E. A. Antonova, I. G. Akhvlediani, and N. A. Slovokhotova, *Vysokomol. Soedinen.*, **B18,** 806 (1976).
14. Y. Hori, T. Kitahara, and H. Kashiwabara, *Radiat. Phys. Chem.*, **19,** 23 (1982).
15. T. Hashimoto, K. Ogita, S. Umemoto, and T. Sakai, *J. Polym. Sci.*, **B21,** 1347 (1983).