

Dielectric Relaxation of Polar Aromatics in Unoriented and Oriented Linear Low-Density Polyethylene

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Received 27 October 1998; accepted 31 March 2000

ABSTRACT: The dielectric behavior of some polar aromatics dissolved in nonpolar unoriented and stretched linear low-density polyethylene was investigated within the temperature region between 150 and 350 K. The measurements were carried out in the frequency range 1 kHz to 10 MHz. The maximum temperatures and the half widths of the loss tangent peaks depend upon the shape and the polar structure of guest molecules. Stretching the samples induced a shift of the loss tangent to higher temperatures, decreased the height, and increased the width of $\tan \delta$ peak. The activation energy is also influenced by the type of guest molecules and orientation of polymer matrix. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1278–1282, 2001

Key words: dielectric relaxation; polar aromatics; molecular shape; linear low-density polyethylene; orientation

INTRODUCTION

Although polyethylene (PE) itself is a nonpolar molecule, one can get a dielectric response either by a slight oxidation of the chains or by doping the polymer matrix with polar molecules as probes.^{1,2} The lower limit of the probe concentration is given by the detection efficiency. Upper limits are set by the probe solubility in the polymer matrix or the deterioration of the mechanical properties. Because dopants of the condensed aromatic type are used, it is not necessary to take care of any effects of electrical conductivity. Debye's equations³ can be applied, describing the dependence of the complex permittivity on the frequency of the driving alternating current (AC) field. The results are presented by using the dielectric loss tangent $\tan \delta$, because the maximum of the $\tan \delta$ curve shows a clear dependence on frequency and tempera-

ture. The main subject of this work is to investigate if and in which way the changes of the $\tan \delta$ curves can be attributed to the structure of the guest molecules and the orientation of the polymer matrix.

EXPERIMENTAL

As host material, a linear low-density polyethylene (LLDPE; Dowlex 2045, Dow Chemical, Dow Europe S.A., 8810 Horgen, Switzerland)^{4,5} was taken. This LLDPE exhibits a density of 0.92 g/cm³ and is a copolymer of ethylene and 1-octene.

The following polar molecules were used (abbreviations in parentheses):

2-bromofluorene (2BFL)

9-bromofluorene (9BFL)

1,2-dibromo-4,5-methylenedioxybenzene
(1D4M)

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Journal of Applied Polymer Science, Vol. 79, 1278–1282 (2001)
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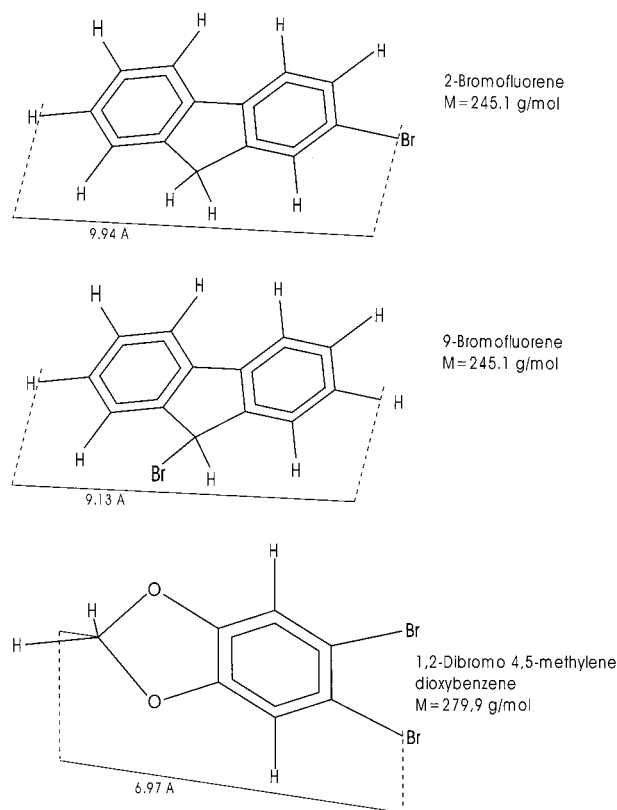


Figure 1 Structure, dimension, and molar mass of 2BFL, 9BFL, and 1D4M.

The structure of the molecules has been outlined in Figure 1.

PE and doping material are weighed in an appropriate ratio and dissolved simultaneously in hot xylene. After evaporation of the solvent, a foil is pressed at 410 K, subsequently quenched in cold water, and kept at a low temperature of about 240 K to prevent the dopant molecules from diffusing out of the PE matrix before measurement.

The undoped LLDPE as well as the pure dopant materials do not show any dielectric loss signal in the frequency and temperature range investigated. Thus the measured losses must originate from isolated dopant molecules, dissolved in the polymer matrix. The concentration of the dopant was varied from 3 to 10 wt % of LLDPE. At the upper limit, scanning electron micrographs show a rough surface of the doped material, indicating partial exclusion of the dopant from the polymer matrix. In the following, the dopant concentration will be expressed by using the number of guest molecules per 1000 host structural units of the form $-\text{C}_2\text{H}_4-$.

In Figure 2, the maximum value of $\tan \delta$ is plotted against the concentration of the guest molecules. The flattening of the curves at higher concentrations originates from mutual dipole compensation by agglomeration of the dopant molecules. For molecular dispersion of probe molecules and for most effective measurement, the optimum concentration turned out to be 6×10^{-3} probe molecules per structural unit. Moreover, at this concentration partial exclusion of the aromatic compounds is not observed. The reported concentration values refer to the entire specimen, but the guest molecules are not present in the crystalline phase.^{2,6} Because the crystallinities exhibit values of about 50%, the real dopant concentration in the amorphous phase will be approximately twice the quoted value.

Dielectric measurements were performed by using a measuring cell from Polymer Laboratories and an impedance analyzer (type 4192 LF) from Hewlett-Packard. A circular piece of foil was mounted between the capacitor plates and cooled down to 160 K by liquid nitrogen. After reaching this start temperature, a computer takes control of the subsequent heating (3 K/min) and records the data. At intervals of 5 K, a sequence of dielectric values is measured by scanning the frequency region from 1 kHz to 10 MHz in eight logarithmically equidistant steps.

The density of doped material shows slightly higher values than that of undoped polymer. This may be explained by the higher densities of the dopants.

At room temperature, a set of samples was stretched up to 500% elongation by using a tensile testing machine (Instron 1121). The birefringence of the doped samples is equal to that of undoped PE (Fig. 3), demonstrating the minimal alteration of host material by the dopant, when using the chosen concentration of guest molecules.

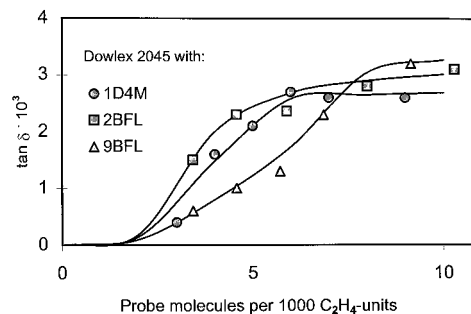


Figure 2 Maximum value of $\tan \delta$ peak in dependence on concentration of probe molecules.

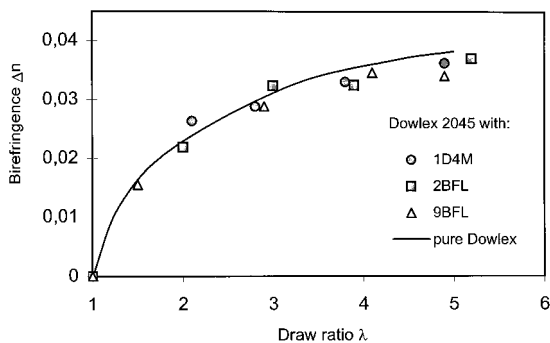


Figure 3 Birefringence Δn as a function of draw ratio λ of undoped and doped (6%) LLDPE samples.

RESULTS AND DISCUSSION

Unstretched PE Samples

In the undeformed state, the polymer matrix possesses random segmental orientation and the PE crystals are arranged in spherulites. The sites of guest molecules are within the amorphous phase between the crystal lamellae.⁷ The probe molecules 2BFL and 9BFL exhibit rodlike shapes, but differ in the direction of their dipole moment, being nearly parallel or perpendicular to the long axis of the molecules, respectively. The rather spherical guest (1D4M) is likely to widen the host's molecular structure and may cause a plasticizing effect.⁸ Measurements for the rodlike probe with the dipole moment \vec{m} along the rod direction yields $\tan \delta(T)$ peaks of smaller line width than for that with \vec{m} perpendicular to the rod axis, whereas the peak temperatures are scarcely shifted (confer Figs. 4 and 5). The \tan

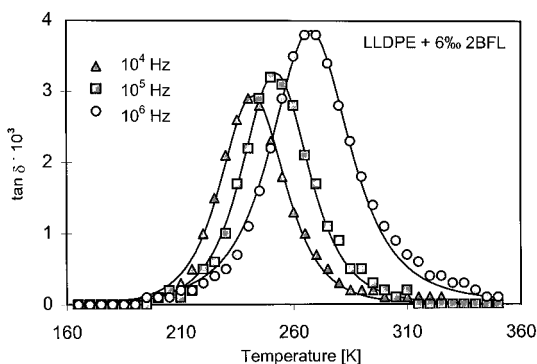


Figure 4 Dielectric loss tangent of unoriented LLDPE doped with 6% of 2BFL in dependence on temperature. The experimental data are fitted by a Pearson VII function in addition to a slightly ascending baseline.

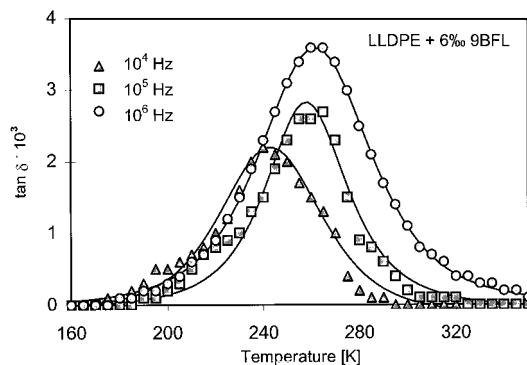


Figure 5 Dielectric loss tangent of unoriented LLDPE doped with 6% of 9BFL in dependence on temperature.

$\delta(T)$ curves of the 1D4M spherical probe molecules show, in addition to line broadening, a marked shift toward lower temperatures (Fig. 6).

For analysis of these two effects (line broadening and temperature shift), the directions of the dipole moments and the mobility of the different guests within the host matrix have to be considered. In the case of 2BFL, the dipole moment \vec{m} is aligned parallel to the rod axis [Fig. 7(b)]. Any change in the direction of \vec{m} relative to the RF field vector \vec{E} is accompanied by rotations about the axis of largest moment of inertia. This is less probable than any orientation change of \vec{m} when fixed perpendicular to the rod axis [Fig. 7(a)]. In other words, in the latter case, the same electric frequency couples to a larger spectrum of oscillations of the host matrix, thus resulting in a broader temperature range, centered, however, around the same peak temperature. If the probe dipole moment is fixed on a more spherical guest

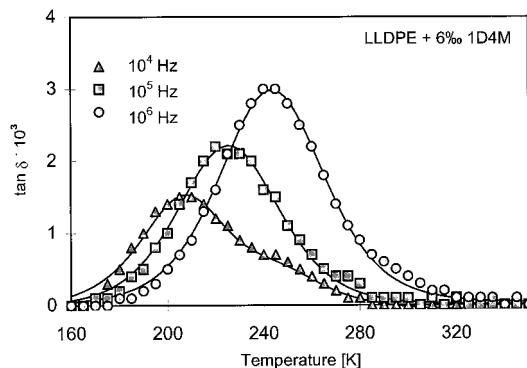


Figure 6 Dielectric loss tangent of unoriented LLDPE doped with 6% of 1D4M in dependence on temperature.

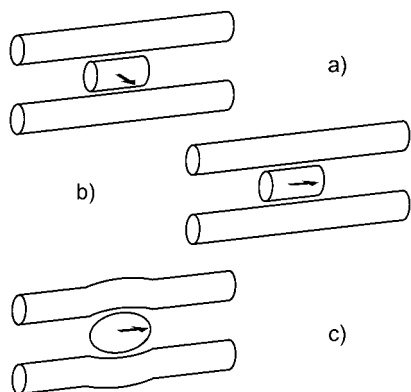


Figure 7 Arrangement of polar probe molecules inside the LLDPE chain molecules: (a) 2BFL; (b) 9BFL; (c) 1D4M.

molecule [Fig. 7(c)], its mobility is enhanced. Additionally, a widening of the host chain structure should result in an increasing decoupling of the chain gliding movements against each other. As depicted in Figure 6, these effects are reflected by peak broadening and a marked shift of peak temperatures toward lower values.

The temperature range of 210–270 K, at which dopant motions lead to maximum loss corresponds to the β -relaxation range of LLDPE, found by dynamic mechanical measurements.^{9–11} This relaxation process can be related to segmental movements in the amorphous parts of semicrystalline LLDPE. In these regions also the dopant molecules are situated. Thus their mobility is coupled to that of the chain segments of the amorphous phase.

Stretched PE Samples

The temperature dependence of the loss tangent at constant frequency (1 MHz) was measured for

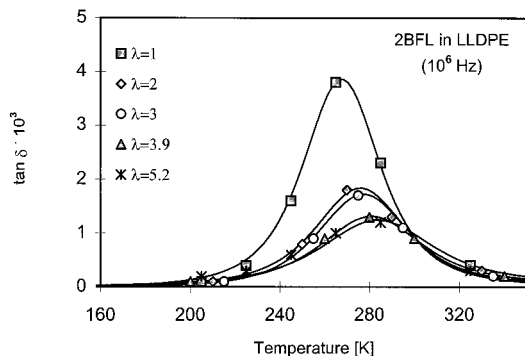


Figure 8 Dielectric loss tangent of oriented LLDPE doped with 6% of 2BFL in dependence on temperature. Parameter: draw ratio λ .

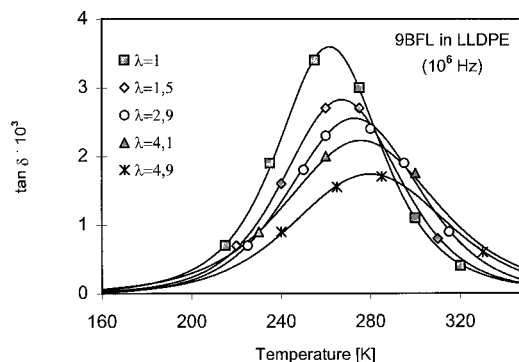


Figure 9 Dielectric loss tangent of oriented LLDPE doped with 6% of 9BFL in dependence on temperature. Parameter: draw ratio λ .

samples stretched to different draw ratios λ and is shown in Figures 8, 9, and 10. The $\tan \delta(T)$ curves of all guest molecules have three features in common: a decrease of peak height, an increase of peak half width, and a slight upward shift of peak temperature with increasing draw ratio.

For the rodlike probes, the activation energies evaluated from Arrhenius plots show a drastic lowering in the oriented samples (Table I).

Without attempting to present a complete description, the following model is proposed to explain the changes of height, half width, and position of $\tan \delta$ peak, as well as the change in activation energy with draw ratio.

When stretching semicrystalline polymers uniaxially, the spherulites are completely destroyed and the crystalline lamellae are reorganized into microfibrils.^{12,13} Polymer molecules that participate in two or more crystallites tend to be oriented along with the microfibrils. During stretching, the polymer chains in the surroundings of the

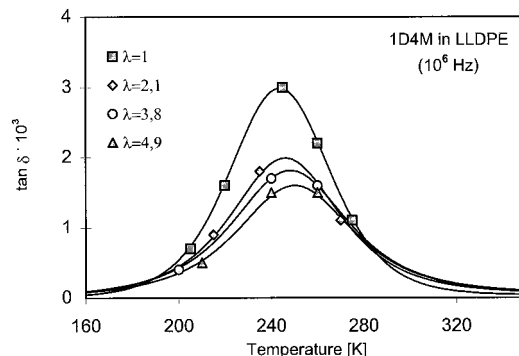


Figure 10 Dielectric loss tangent of oriented LLDPE doped with 6% of 1D4M in dependence on temperature. Parameter: draw ratio λ .

Table I Activation Energies for Oriented and Unoriented Samples

Probe	2BFL		9BFL		1D4M	
	1	5.2	1	4.9	1	4.9
Draw Ratio λ	1	5.2	1	4.9	1	4.9
Activation energy (kJ/mol)	129	25	29	17	50	47

host molecules are oriented, and thus oscillations or rotations of probe dipole moments are more and more restricted. The restrictions of polymer chain movement, imposed by orientation, shift the onset of interchange of probe molecule sites to higher temperature. The long axes of probe molecules and polymer segments become more parallel, suppressing numerous translational and rotational motions of the probe molecules, while favoring rotations about their long axes. This will lower the activation energy corresponding to the observed relaxation process and will also flatten and broaden the $\tan \delta$ peak. This mainly phenomenological model has to be verified on the basis of more detailed investigations, taking into consideration for example the exact variation of height and half width of the $\tan \delta$ peak and the temperature shift of the peak in dependence on draw ratio.

CONCLUSION

Doping PE films with polar probe molecules of the condensed aromatic class, differing in shape and direction of dipole moment, allowed dielectric investigation of relaxation processes in PE. Measurements could also be performed on samples stretched to various draw ratios. For the interpretation of the relaxation process, two features have to be taken into account: first, the interaction between motions of polymer segments and probe molecules (depending on sample orientation and

probe molecule shape), and second, the influence of the dipole moment direction within the probe molecule. Qualitatively, the following experimental observations could be explained:

in unoriented samples, a more globular probe molecule causes a larger half width of $\tan \delta$ peak and a shift of peak maximum temperature to lower values than a rodlike probe.

in stretched samples, with increasing draw ratio, the $\tan \delta$ peak shifts to higher temperatures and its height decreases, whereas its half width grows.

the activation energy of rodlike probes in stretched samples decreases with increasing draw ratio.

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