

Dielectric and Fluorescent Probes to Investigate Glass Transition, Melt and Crystallization in Polyolefins

Otto van den Berg, Wolter F. Jager, Wilco G.F. Sengers, Michael Wübbenhorst, and Stephen J. Picken

Department of Polymer Materials & Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands, The Dutch Polymer Institute

INTRODUCTION

Dielectric spectroscopy is versatile technique, which has been used extensively for the study of molecular dynamics in many polymers [1]. The dynamic range of more than 15 decades enables the study of fluctuations in dipoles and the diffusion of dipoles on different length scales, ranging from molecular bond rotations up to the relaxation dynamics of entire polymer molecules. A prerequisite for the application of dielectric spectroscopy is the presence of dipoles, which provide the link between the molecular motions and the external electrical field. There is however a substantial class of non-polar polymers, like polyolefins, which do not have dipoles. In this paper we introduce a new method to make non-polar polymers dielectrically active by addition of (4,4'-(*N,N*-dibutylamino)-(*E*)-nitrostilbene (DBANS, figure 1).

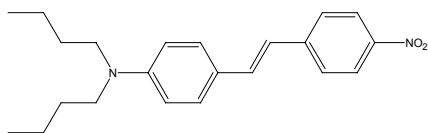


Figure 1. Structure of (4,4'-(*N,N*-dibutylamino)-(*E*)-nitrostilbene

In addition to the special dielectric properties of DBANS we also made use of its fluorescent properties. Charge transfer probes, like DBANS, have been used extensively as fluorescent probes for monitoring polymerization processes and for polymer characterization [2-10]. Temperature dependent emission is recorded in order to find out how the probe fluorescence is related to polymer dynamics. This will reveal to what extent dielectric response and fluorescence response provide equivalent or complementary information on the changes in the polymer mobility, particularly at the glass transition or during melting/crystallization.

RESULTS

The main feature of DBANS is its ability to specifically detect segment mobility in a range of polymers. In figure 2 the dielectric loss for undoped LDPE and three LDPE/DBANS mixtures is shown. The dielectric β -process, which is associated with the glass transition, is specifically enhanced. The γ -process, associated with a local crankshaft motion in the polymer chain, is not influenced. In figure 3 the Arrhenius plots for (doped) LDPE, *i*-PP and PS are shown. For *i*-PP and PS the relaxation time τ_α is practically independent on probe concentration in the range of 0.1 – 1.0%, which means that the probe reorientation is closely coupled to the segmental relaxation. For LDPE a shift towards shorter relaxation times in doped polymer is found. This indicates DBANS preferentially probes the more mobile parts of the amorphous phase. A linear relationship was found between probe concentration and the relaxation strength $\Delta\epsilon$ up to 0.5% probe content, which proves DBANS does not phase separate up to this concentration.

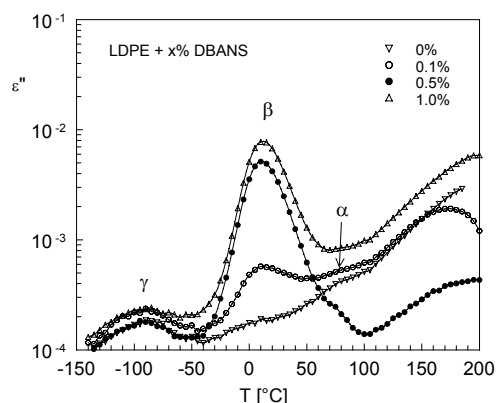


Figure 2. Dielectric loss $\epsilon''(T)$ at $f = 13$ kHz for undoped LDPE and three LDPE/DBANS blends

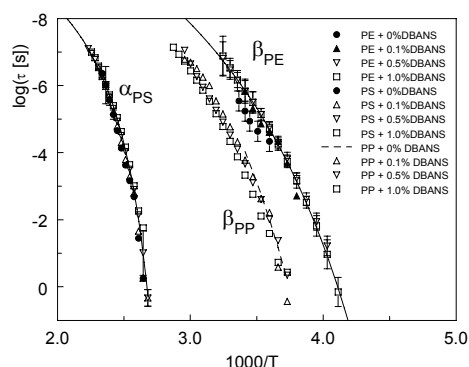


Figure 3. Arrhenius representation of the primary relaxation time for undoped and DBANS-doped PS, *i*-PP and LDPE samples

Temperature dependent fluorescence measurements on LDPE and *i*-PP didn't monitor the glass transition. The crystallization however, was clearly detected as a pronounced red-shift in the fluorescence of the added probe. This red-shift is caused by migration of probe from the crystallizing regions, resulting in a local increase of probe concentration. In figure 4 the real time fluorescence data for *i*-PP at two different cooling rates is shown. For different cooling rates, as expected, the onset and the end of the crystallization process are clearly visible and show excellent correspondence with DSC measurements performed on the same samples under identical conditions. The melting is observed as a change in gradient accompanied with a small bump.

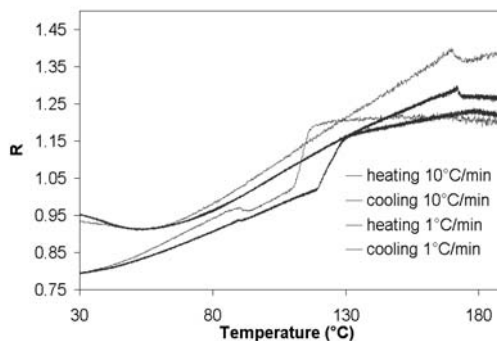


Figure 4. Real time intensity ratio $R (I_{578}/I_{605})$ for *i*-PP doped with 0.5% DBANS as a function of temperature.

In order to mimic the increase in probe concentration during crystallization, the temperature dependant emission spectra of DBANS in paraffin oil were recorded. The results are shown in figure 5. The emission is particularly sensitive to changes in concentration between 0.5 and 1%. This corresponds well with the expected changes in local probe concentration during crystallization of *i*-PP. The qualitative correlation between the paraffin oil model system and the real time measurements is remarkable since probe distribution in the polymer will be inhomogeneous and influenced by the rate of diffusion. In addition the high viscosity of the model system might influence the emission in a manner not covered by the model system.

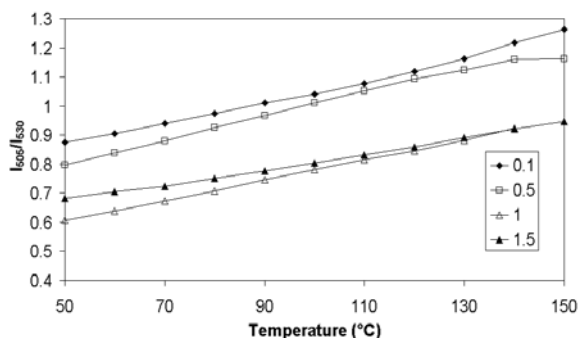


Figure 5. Intensity ratio I_{505}/I_{530} for paraffin oil at different concentrations of DBANS as a function of temperature

CONCLUSIONS

Due to the lack of internal rotational degrees of freedom of the probe molecule, large fluctuations of the polar axis of the rigid rod-type probe are effectively coupled to the cooperative dynamics of the matrix. Local dynamics and dynamics involving the crystalline phase do not show up in the dielectric response. Addition of DBANS specifically enhances the strength of the dielectric glass transition process. The "strengthening" is proportional to the mean probe concentration up to 0.5% DBANS.

Our results show DBANS is an excellent dielectric probe for the study of cooperative dynamics in polyolefins.

Fluorescence spectroscopy on DBANS doped LDPE and *i*-PP can be effectively used to detect both crystallization and melting. The observed changes in probe emission are explained by migration of probe molecules; from the crystallizing regions during crystallization and into the melting regions during melting. These migrations, leading to concentration increase and decrease, respectively, were proven with dielectric spectroscopy.

It was shown that a change in local probe concentration is the major contributor to the spectral change, taking place during crystallization.

EXPERIMENTAL

The polymers were received from Shell (PS, Shell N7000) and Sabic Stamylnan (LDPE, Sabc 2100TN00, MFI 0.3; *i*-PP, Sabc 11E10, MFI 0.3). Polystyrene was purified by a triple precipitation from dichloromethane/methanol. *i*-PP and PE were used as received. Mixtures of polymer with DBANS were prepared by melt mixing in a 20 cc Brabender batch mixer at 200°C. Thin sheets of doped polymer were prepared by hot pressing using 0.3 mm aluminum spacers and were used for fluorescence and DSC measurements. From these sheets squared pieces of 1 cm² were cut and pressed together with 100 μm glass fiber spacers between circular brass electrodes (Ø = 2cm) resulting in samples with a well-defined geometry for DRS experiments.

Dielectric relaxation spectroscopy

Dielectric experiments were performed using a high precision dielectric analyzer (ALPHA analyzer, Novocontrol) in combination with a Novocontrol Quatro temperature system providing control of the sample temperature with an accuracy better than 50mK. All dielectric measurements were performed in the frequency range from 10⁻¹ to 10⁷ Hz. Temperature dependent experiments were realized by consecutive isothermal frequency sweeps in the temperature range from +200°C to -120°C in steps of -5K, which resulted in an effective cooling rate of about 0.5 K/min. In order to determine the relaxation time $\tau(T)$ from the dielectric loss curves we have fitted the frequency spectra $\epsilon''(\omega)$ by the empirical Havriliak-Negami relaxation function (eq. 1) using the Levenberg-Marquardt algorithm:

$$\epsilon'' = -\text{Im} \left\{ \frac{\Delta\epsilon}{\left(1 + (i\omega\tau)^a\right)^b} \right\} + \frac{\sigma}{\epsilon_0\omega} \quad (1)$$

Here $\Delta\epsilon$ and τ correspond to the relaxation strength and the mean relaxation time of the relaxation process. The two shape parameters a and b , which determine the logarithmic slope of the low frequency loss tail a and the high frequency loss tail $-a \cdot b$, are determined by the underlying distribution in relaxation times. The second term in eq. 1 accounts for ohmic conduction.

Fluorescence spectroscopy

Fluorescence spectra were recorded with a Spex/Jobin-Yvon Fluorlog 3 fluorescence spectrometer equipped with a fiber optic cable in combination with a Linkam hot stage, which was kept under a stream of dry nitrogen during the experiments. Temperature dependent measurements were carried out isothermally in steps of 10K in cooling from +150°C to -100°C at 10°C per minute. Fluorescence experiments using DBANS were carried out with an excitation wavelength of 400 nm. The angle of the incident beam was kept at 45° to the plane of the sample in order to minimize back reflection of excitation light. The emission spectra, corrected for the wavelength dependent sensitivity of the photo multiplier tube, were recorded with wavelength intervals of 1 nm. Real time fluorescence was recorded on an SGL/Oriel CM1000 cure monitor. Freshly prepared samples were heated to 190°C at the chosen heating rate, held at 190°C for 5 minutes and subsequently cooled to 30°C.

REFERENCES

1. Kremer, F. *Broadband Dielectric Spectroscopy*; Springer-Verlag: Berlin Heidelberg New-York, 2002.
2. Loutfy, R. O. *Macromolecules* **1981**, *14*, 270-275.
3. van Ramesdonk, H. J.; Vos, M.; Verhoeven, J. W.; Mohlmann, G. R.; Tissink, N. A.; Meesen, A. W. *Polymer* **1987**, *28*, 951-956.
4. Paczkowski, J.; Neckers, D. C. *Macromolecules* **1992**, *25*, 548-553.
5. Jager, W. F.; Lungu, A.; Chen, D. Y.; Neckers, D. C. *Macromolecules* **1997**, *30*, 780-791
6. Jager, W. F.; Volkers, A. A.; Neckers, D. C. *Macromolecules* **1995**, *28*, 8153-8158.
7. Vatanparast, R.; Li, S. Y.; Hakala, K. *Macromolecules*, *33*, 438-443.
8. Jager, W. F.; Norder, B. *Macromolecules* **2000**, *33*, 8576-8582.
9. Peinado, C.; Salvador, E. F.; Catalina, F.; al., e. *Polymer* **2001**, *42*, 2815-2825.
10. Jager, W. F.; van den Berg, O. In *ACS Symposium series*; Belfield, K. D., Crivello, J. V., Eds.; American Chemical Society: Washington D.C., 2003; Vol. 847, pp 426-436.