ABSTRACT

The present study examines the structure – properties relation of hybrid nanostructured systems of hyperbranched polyimides (HBPI) produced using the monomers 2,4,6-triaminopyrimidine (TAP) and 4,4′-oxydipthalic anhydride (ODPA) cross-liked by copolymerization with ethylene glycol diglycidyl ether (EGDE) in different degrees. Specimens with degrees of cross-linking 0%, 5%, 10%, 15%, 20%, 25%, 30%, 35%, 50%, 75% and 100% were prepared in Prague by the Czech Research Group consisting of Petr Sysel, Jiří Kotek and Radka Hobzova, using the two-stage method for polyimide synthesis, resulting in thin trasparent films of 0.03-0.1mm think. The specimens are named S***xx*** were ***xx*** is a number corresponding to a particular cross-linking percentage.

The fundamental aim of this study is the development of polyimides to be used in the future for gas separation in petrochemical industries and other facilities. Low permeability is observed for common linear polyimides, leading all researches to seek methods increasing the free volume to these materials. Branching and cross-linking by copolymerization with flexible monomers is believed to be an answer to the problem which is studied at this particular work.

Specimens are observed by means of dielectric spectroscopy such as dielectric relaxation spectroscopy (DRS) and the technique of thermally stimulated depolarization currents (TSDC). DMA and DSC experiments at the same specimens were also curried out by foreign researchers. Results have shown the existanse of a α-relaxation and γ-relaxation as well as conductivity phenomena which are all studied.

An α-relaxation, associated with the glass transition, is observed as a peak in TSDC method, while in DRS measurements it is masked by conductivity and is visible as a shoulder, only in some cases. Usually one glass transition temperature is recorded with TSDC, except for specimens S15 and S30 showing two peaks. The general pattern of the T_g diagram vs cross-linking is followed by all techniques utilized for Tg monitoring, indicating decrease of T_g value for S00 to S35 specimens and then a form of stability against cross-linking increment. Other thermoanalytical techniques such as DSC and DMA report greater values of T_g. DSC records two T_gs giving T_{g1} (lower ΔC_p and lower Tg values) values near to that of TSDC method.Therefore it is our belief that TSDC (as every other method) helps as record only one of the two ways of glass transition.

Shown only in DRS spectra, γ-relaxation is observed and analysed by mathematical interpolation of Cole-Cole equation. The mechanism of γ-relaxation is attributed to dipolar topic movements of imide cycles on polyimide chain. It was found that the γ-relaxation mechanism becomes slower and stronger as the cross-linking degree increases. As for the shape of dielectric response, the pick of the mechanism becomes more intense as cross-link increases. Comparing the results with the linear PI, the sub-glass transition relaxation in HBPI is faster and more intense in comparison to γ-relaxation of linear PI suggesting increase of free volume in the HBPI.

Further studies of DRS spectra, indicated the existence of the so-called CCR mechanism (conductivity current relaxation) overlapping a fade CR-relaxation (conductivity relaxation). These conductivity phenomena are results of a special type of morphology in the bulk of polyimides, were regions with different conductivities block current carriers and form interfaces polarized by the external field as shown in DRS spectra for the greater temperatures. It is hoped that more important information

about the morphology of these regions will be acquired by water diffusion experiments.

Keywords

Hyperbranched polyimides (HBPI), cross-linking, 2,4,6-triaminopyrimidine (TAP), 4,4′-oxydipthalic anhydride (ODPA), ethylene glycol diglycidyl ether (EGDE), dielectric relaxation spectroscopy (DRS), thermally stimulated depolarization currents (TSDC), glass transition, γ-relaxation, α-relaxation, conductivity current relaxation (CCR), water absorption .