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Study of diffusion coefficient of water and homologous series of primary alcohols in PEBA membranes by NMR

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1. Introduction

Today in many technical and pharmaceutical processes the transport of small molecules like solvents, gases, or drugs in polymers is a central topic of investigation. For example the transport of solvent molecules in nanofiltration applications, the methanol transport in direct methanol fuel cells (DMFC) and the rate-determining step for drug delivery are dependent on the diffusion characteristics of polymer materials. Especially for membrane processes where the properties of the polymer membrane strongly depend on its permeability and selectivity, the relative solubility and the diffusivity of solvent and solute in the membrane play the major role.[1-3]
For membranes, in the sense of dense polymeric films, the interaction between polymer structure and crystallinity on the microscopic level on one hand and the solvent on the other hand should be under investigation to understand the mechanism of membrane selectivity. One of the parameters is the diffusion of a component in a membrane related to its-diffusion coefficient. This partial self-diffusion coefficient reflects the translational motions of solvent molecules in the polymer matrix. Between diffusivity and concentration of the solvent molecules in the material (swelling) a correlation can be obtained.[4] This correlation depends on the structure and the chemical nature of the polymer, and varies for various polymers extensively concentration dependent.

2. Experimental Results

Thermal properties of the cast PEBA polymer films were determined by DSC. According to the literature[5], two glass transitions (T_g) and two melting point temperatures (T_m) are expected. The first T_g for all block copolymers at lower temperature is not detectable in our measurements. However, the first T_m for all copolymers in the low temperature range for 8 - 16 °C is observed and assigned to the fusion process of polyether blocks. The second T_g and T_m around 50 – 106 °C and 130 – 225 °C, respectively, belong to the glass transition and fusion process of polyamide blocks.

The mobility of the guest molecules diffusing through a polymer is dependent on the affinity between the diffusing-component and the polymer. It is related to many factors such as chain mobility, polarity, crystallinity, thermal or processing history, molecular weight, temperature, free volume, etc.[6] The diffusion of water and a homologous series of primary alcohols in various membranes from polyether-*block*-polyamide (PEBA) multiblock-copolymers are studied by pulse field gradient stimulated spin-echo sequence nuclear magnetic resonance (PFG-STE-NMR). It is shown that this technique is very sensitive for the study of such dense polymer films, provided they can be measured without further treatment. The materials cast from solution differ both by chemical

composition and casting solvent (cyclohexanol and 1-butanol), and are characterized by differential scanning calorimetry (DSC) in order to correlate the transport properties of diffusivity with the two-phase nanostructure of the membranes generated from soft and hard domains. It is found that the diffusion coefficient varies as a function of the casting solvent and is lower in membranes with lower crystallinity. Samples containing a polyamide-12 (PA_{12}) block exhibit a higher diffusion coefficient for ethanol, if the polyether block is made from poly(tetramethylene oxide) (PTMeO) as compared to materials with a poly(ethylene oxide) (PEO) polyether block. If, on the other hand, the molar fraction of a PEO polyether block is kept constant, but the polyamide block is exchanged, materials containing polyamide-6 (PA_6) show higher diffusion coefficients for the entire series of homologous primary alcohols studied, as compared to copolymers containing PA_{12} blocks. The decrease of the diffusion coefficient follows the polarity of the diffusing-component in the following order of PEBA grade: 57PEO/PA6 > 55PEO/PA12.

3. Conclusions

The PFG-NMR technique has been shown to be a very sensitive technique for the study of diffusion coefficients in dense polymer films which can be measured directly without further treatment. Its limitation lies in material systems with very high degrees of swelling or which cannot incorporate enough diffusing component. If the samples reach a high degree of swelling the diffusion coefficient of the agent reaches mostly the value of the free agent. For the *polyether-block-polyamide* copolymer (PEBA) the diffusion coefficient of a homologous series of alcohols and water varies with changes in the casting solvent. As the diffusion coefficient for membranes with lower crystallinity is also lower than for membranes with high crystallinity the diffusion mechanism seems to be influenced mostly by the chemical structure of the blocks. Additionally, it can be suggested that the interaction between the polar polyamide block and the diffusing-component such as water and a series of primary alcohols influences the transport properties.

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