FIR SPECTRA AND REGULARITY OF COPOLYMERS

P.Nikolić+*, I.Božović++*, I.Javni**, D.Todorović+, D.Raković+*
and D.Fleš[x]

+Faculty of Electrical Engineering, Belgrade

* Institute of Physics,Belgrade

++ Department of Physics,Fac.of Sciences, Belgrade

** Faculty of Technology, Tuzla

[x] INA- Res.& Develop. Dept., Zagreb

In this communication we present far-infrared (FIR) spectra of the α-methyl styrene - malein anhydride copolymer, which in our opinion provide further support to some earlier conclusions [1] about regularity of this copolymer.

In general, copolymers are either regular (alternant) as represented by ..ABABABAB.. or stochastic, say ABBABBBAAB... Regularity has significant influence on physical and chemical features (such as crystallinity, mechanical strength, resistance against chemical agences, etc.) of copolymers [2]. One important method to obtain regular sequences is copolymerization in charge-transfer (CT) systems, realized either via cross-propagation or via homopolymerization of CT- complexes [3]. Shirota [4] has surmised that both reactions in fact take place, their relative contributions depending on the concentrations of comonomers, initiator, temperature, etc.

Correctness of Shirota's model has both fundamental and practical significance: varying the mentioned parameters one could favorize one of the two possible reactions and thus control the speed of the copolymeruzation and the features (in particular, regularity) of the product. Experimental kinetical studies of

Fleš and coworkers [5] have confirmed Shirota's assumption, for a series of regular CT-type copolymers. Regularity of the copolymers was assumed in these studies: experimental support was found in equal amount (to within 0.1%) in the product copolymer, regardless of their starting relative concentration in the solution. One should also mention that the comonomers were chosen which do not homopolymerise themselves (under the same conditions). However, central importance of regularity of the copolymers in these studies has motivated us to look for an independent, physical test, and this we have found in the FIR spectra.

In general, one should expect to observe in far-infrared region the out-of-plane skeletal vibrations of the polymer, whose frequencies and relative intensities should differ for alternant and stochastic copolymers, respectively. In particular, if the relative amounts of comonomers in the copolymer are varied, some spectral lines would gain and others would lose in intensity. Thus, if one finds identical spectra for a series of copolymers prepared from solutions with different relative concentrations of comonomers it would be a strong indication of the regular, alternant structure. An unambiguous answer, in our opinion, requires however, assignated spectra and normal mode analysis.

In this communication the object of our investigation was a copolymer of α- methyl styrene (α- MS) and malein anhydride (MA). The first, α-MS, is oily colourless liquid (at room temperature); chemical bruto formula is $C_6H_5(CH_3)C = CH_2$; molecular weight is 118,18 a.u.. MA is white powder; formula is $C_4H_2O_3$ and m.w. is 98,06 a.u.; when it is dissolved in benzene a colourless liquid is obtained. Addition of α- MS to such a solution produces however a bright-yellow liquid (for $60^{o}C < t < 90^{o}C$), indicating strongly formation of CT complexes; this is fully supported by NMR results. In these complexes MA is an electron acceptor and α- MS is an electron donor; active part of both comonomers are double C=C bonds. The product of copolymerization is white powder with molecular weight about 35.ooo a.u; comonomers participate in the ratio 1:(1± 0,001) as found bv quantitative elementary chemical analysis and also by conductometric measurements [1]. As found in these kinetical studies both reactions are possible, with complex homopolymerization dominant at greater total comonomer concentrations, equimolar relative concentration and inert solvents. Cross-propagation is favourised at lower total concentration, higher relative concentration of less active comonomer (i.e. α- MS) and active solvents.

EXPERIMENTAL: Twenty seven samples of α-MS-MA copolymer were prepared, with relative comonomer concentrations 1:9, 2:8, ..., 9:1 and total comonomer concentrations of 1,2 and 3 mol/l. Five representative samples were chosen (I:1 mol/l, 40% MA and 60% α-MS; II: 1 mol/l, 80% MA and 20% α-MS; III: 3 mol/l, 20% MA and 80% α-MS; IV: 3 mol/l, 40% MA and 60% α- MS; V: 3 mol/l, 80% MA and 20% α-MS), and pressed to produce pills for spectroscopic analysis. The FIR transmission spectra were recorded for each of them (at room temperature) on Beckman FS-720 Fourier FIR spectrometer, in 40-400 cm^{-1} region. These spectra are reproduced in Fig. 1; different scales for transmission coefficient are used to avoid overlapping of the spectra. Although all of the pills were not of the same width, it is clear from Fig. 1 that qualitative features (i.e. position and shape of the lines) are identical for all five samples. Thus one concludes that regular copolymers dominate in each of these samples, in accordance with chemical analysis and conductometric results [1].

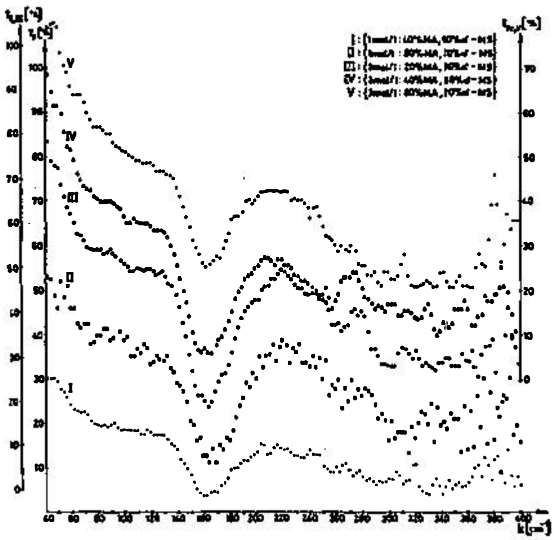

Fig. 1

Further investigation of this problem is in progress. This will include larger number of samples of increased purity, low-temperature spectra, polarised spectra of oriented samples, spectra of copolymer in solution. In addition, normal mode analysis will be attempted, to assignate the spectra. Finally, via numerical experiments a quantitative estimation of the presence of irregularities in a predominantly alternate copolymer might be achieved.

References:

[1] Javni I.and Fleš, D., Proc. 6 th Yug. Symp.Pure & Appl. Chem.
[2] Furukawa J. and Kobayashi E., Rubber Chemistry and Technology 51 (1978) 600.
[3] Tschuchida F. and Tómano, T., Macromol, Chem. 141 (1971) 265.
[4] Shirota Y. et al., Macromolecules 7 (1974) 4.
[5] Fleš D., Vuković R. and Kurešević D., Polymer Bulletin 2 (1980) 527., J. Polym. Sci. Polym. Chem. Ed. 17 (1979), 1839., 3835.