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Intramolecular Charge Transfer Complexes 5.

Poly(N-(2-Hydroxyethyl) Carbazolyl Methacrylate – Co – 2,4-Dinitrophenyl Methacrylate)

Cristofor I. Simionescu, Virgil Percec and Almeria Natansohn

"Petru Poni" Institute of Macromolecular Chemistry, 6600 Jassy, Rumania

Summary

Copolymerization of N-(2-hydroxyethyl) carbazolyl methacrylate (M_1) with 2,4-dinitrophenyl methacrylate (M_2) takes place through the simple terminal mechanism having the parameters $r_1 = 0.35$ and $r_2 = 0.53$. Intramolecular charge transfer complexes with different donor/acceptor ratios are obtained. The intramolecular complexation is correlated with the alternating diad fraction and with the copolymer conformation through the ^{1}H-NMR spectra registration temperature.

Introduction

The picryl methacrylate (acceptor monomer) copolymerization with different donor monomers: N-(2-hydroxyethyl) carbazolyl methacrylate (1), N-(2-hydroxyethyl) carbazolyl acrylate (2), N-ethyl-3-hydroxymethyl carbazolyl methacrylate (3), 1-(2-fluorenyl) ethyl methacrylate (3) and 2-naphthyl methacrylate (4) leads to intramolecular charge transfer complexes copolymers with up to 30-40% acceptor structural units in the chain.

2,4-dinitrophenyl methacrylate (5) is a weaker acceptor but, unlike picryl methacrylate, can homopolymerize. Consequently, this acceptor monomer can generate copolymers with all possible compositions.

The aim of this paper is to study an intramolecular charge transfer complex obtained by copolymerization of N-(2-hydroxyethyl) carbazolyl methacrylate (M_1, HECM) with 2,4-dinitrophenyl methacrylate (M_2, DNPM).

Experimental

HECM (1) and DNPM (5) were prepared according to the described methods and characterized by elemental analysis and spectral methods. Copolymerizations were performed in dioxane at 60°C, under argon, with AIBN (1% from monomers) as initiator. Copolymerization data are given in Table 1. The total monomers concentration was in all cases 0.5 M. The copolymers were separated by precipitation with methanol and purified by reprecipitation from dioxane solutions with methanol. Copolymer compositions were determined from ^{1}H-NMR spectra registered in DMSO-d_6 at 60°C by different ratios of the aromatic region signals, or including the $-CH_2-CH_2-$ signal from HECM (Figure 1).

Table 1
Copolymerization data

Sample	F_1	Time (hr)	Conversion (%)	f_1
1D	0.9	1.75	2.23	0.81
2D	0.8	4.0	5.25	0.68
3D	0.7	4.75	5.13	0.60
4D	0.6	5.0	3.57	0.53
5D	0.5	7.0	5.66	0.47
6D	0.4	8.0	5.24	0.41
7D	0.3	8.5	4.47	0.34
8D	0.2	8.75	3.21	0.26
9D	0.1	12.75	5.40	0.14
poly(DNPM)	0	12.75	4.80	0

F_1 = molar fraction of HECM in the initial mixture
f_1 = molar fraction of HECM in copolymer

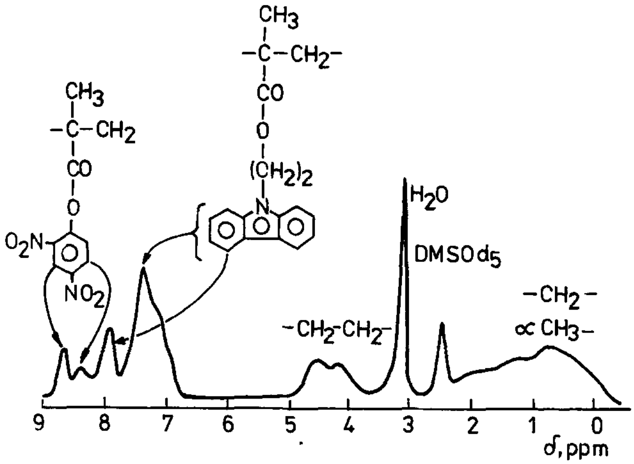

Figure 1. ^{1}H-NMR spectrum of sample 5D

The ^{1}H-NMR spectra were registered on a JEOL C-60HL spectrometer, and the UV-Visible spectra on a Unicam SP 800 spectrophotometer (tetrahydrofuran solutions).

Results and Discussions

The composition of the intermonomeric charge transfer complex is proved to be 1:1 by Job's method (6).

The copolymerization diagram is given in figure 2. Analysing the copolymerization data by Kelen-Tüdös equation (7)($\alpha = 1.2$), one obtains the straight line in figure 3.

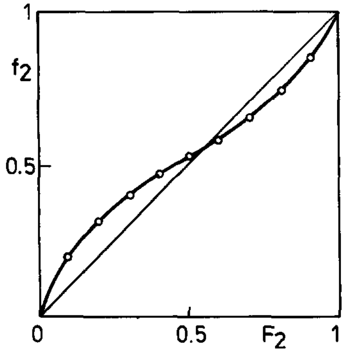

Figure 2. Copolymerization diagram

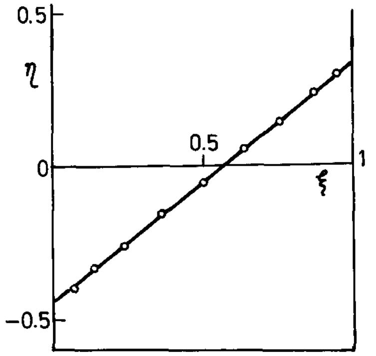

Figure 3. The Kelen-Tüdös plot

Unlike all systems studied by us, in this case the intermonomeric complex seems to play a minor part in the copolymerization mechanism, because no curvature is observed in the Kelen-Tüdös plot. This is an evidence of the validity of the simple terminal model, characterized by the reactivity ratios:

$$r_1 = 0.35 \qquad r_2 = 0.53$$

These values are used for diad fractions calculation, according to Harwood's algorithm (8).

The obtained copolymers are soluble in dioxane, tetrahydofuran, dimethylformamide, dimethylsulphoxyde and only 1D-3D samples are soluble in chloroform. All copolymers are yellow-coloured, the intensity of the colour growing and becoming light-brown when increasing alternant sequences.

The intramolecular character of the charge transfer complex copolymer is demonstrated by the linear dependence of the charge transfer absorption band in the visible domain on concentration for electronic spectra.

The charge transfer complex concentration depends on the probability of placement of donor and acceptor groups in the most favourable position. For this reason, the charge transfer absorption band is correlated with 12 diad fraction. As it can be seen in figure 4, the absorption maximum is the same with the maximum of 12 diad fraction, and this demonstrates the intramolecular complex concentration dependence on sequence distribution.

The ^{1}H-NMR spectra registered in dioxane at room temperature evidence a shift of the aromatic protons of DNPM units to higher fields when increasing the HECM content in copolymer. The same phenomenon is observed in the spectra registered in $CDCl_3$, but the copolymer solubility is very poor when increasing the DNPM content in copolymer, beginning with 4D sample. The chemical shift of the 3 aromatic proton from DNPM units (the most deshielded one, being therefore easier to be measured) was represented against the DNPM fraction from the alternating diads (because $f_2=f_{22}+\frac{1}{2}f_{12}$, this fraction is calculated with the relation $\frac{1}{2}f_{12}/f_2$). This correlation is a straight line represented in figure 5, and is another evidence for the complexation dependence on sequence distribution.

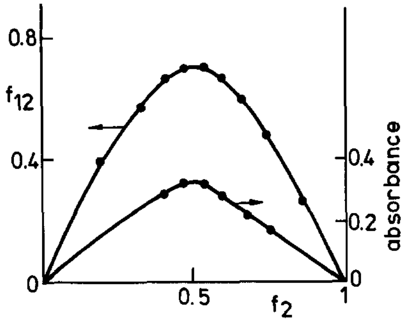

Figure 4. Diad 12 fraction and charge transfer absorption band (at λ = 450 nm) against copolymer composition

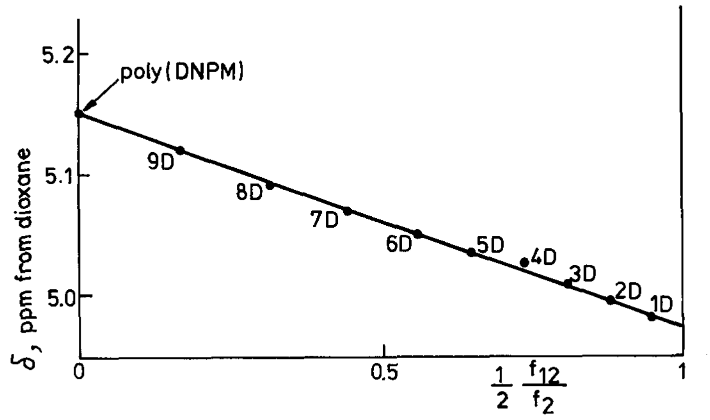

Figure 5. Chemical shift of 3-rd aromatic proton from DNPM structural units against $\frac{1}{2}f_{12}/f_2$

The conformation influence on intramolecular complexation is evidenced by registering the ^1H-NMR spectra at different temperatures. The 3-rd aromatic proton signal from DNPM shifts to higher fields when decreasing the registration temperature. This demonstrates the decomplexation due to thermal motions when increasing the temperature. Figure 6 gives this region of the 2D sample spectrum registered between -20 and 60°C. Unfortunately, when decreasing temperature, the solution viscosity increases and the signals broadens very much.

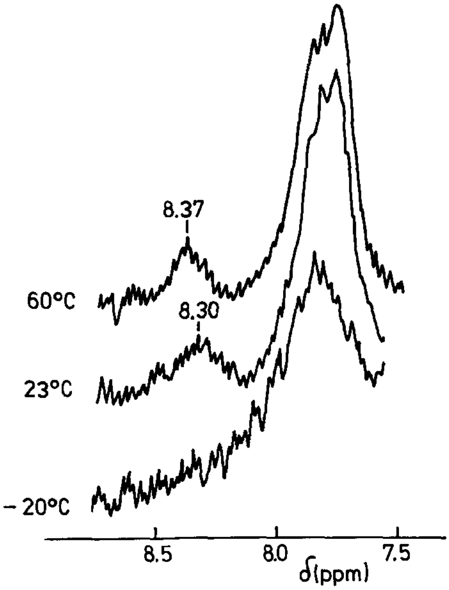

Figure 6. ^{1}H-NMR spectrum (aromatic region) of sample 2D in $CDCl_3$

In conclusion, HECM and DNPM copolymerize through a mechanism where the intermonomeric complex contribution can be neglected. Intramolecular charge transfer complexes having different donor/acceptor ratios are obtained. The intramolecular complex concentration depends on sequence distribution and copolymer conformation.

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