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Intramolecular Charge Transfer Complexes

12. Poly[N-(2-Hydroxyethyl)Carbazolyl Acrylate-Co-2'-Ethyl-Acryl-4,5,7-Trinitro-9-Fluorenone-2-Carboxylate]

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SUMMARY

An intramolecular charge transfer complex (CTC) was obtained by radical copolymerization of N-(2-hydroxyethyl)carbazolyl acrylate with 2'-ethylacryl-4,5,7-trinitro-9-fluorenone-2-carboxylate. The copolymerization mechanism is simple terminal, and the obtained CTC does not present decomplexation even at high temperatures. This is the first intramolecular CTC containig both carbazole- and trinitrofluorenone-substituted structural units.

INTRODUCTION

Radical copolymerization of electrono-donor and electrono-acceptor monomer pairs leads to intramolecular charge transfer complexes (CTC) (1-13) when the steric positions of the electrono-donor and electrono-acceptor groups premit the complexation. For the donor and acceptor groups directly bonded to the main chain, this condition is realized only for coisotactic alternating sequences (1-10). This condition is not necessary for the copolymers with increased distance between the complexing group and the main chain (11,12). This paper presents preliminary data on the first enchainment in a copolymer intramolecular CTC of structural units having carbazole and trinitrofluorenone as substituents. This CTC is obtained by copolymerization of N-(2-hydroxyethyl)carbazolyl acrylate (HECA, M_1) with 2'-ethylacryl-4,5,7-trinitro-9-fluorenone-2-carboxylate (ETNFA, M_2).

EXPERIMENTAL

HECA was synthesized as previously described (5). ETNFA was synthesized like 2'-ethylmethacryl-4,5,7-trinitro-9-fluorenone-2-carboxylate (ETNFM)(14-16), according to the reaction scheme :

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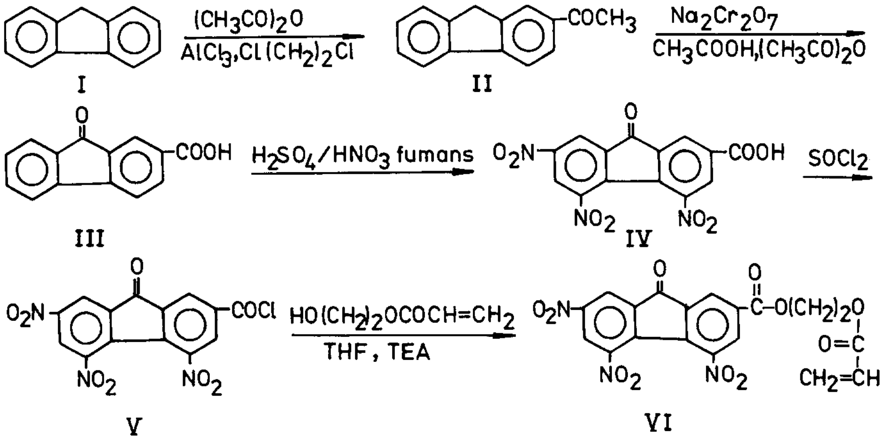

After testing some methods given in the literature, the following were chosen : 2-acetylfluorene (II) was most conveniently synthesized (yield 100%) according to Sulzberg and Cotter (17). Without purification, 2-acetylfluorene was oxydized to 9-fluorenone-2-carboxylic acid (III) according to Turner and Stolka method (15). The synthesis of 4,5,7-trinitro-9-fluorenone-2-carboxylic acid (IV) was realized using the method proposed by Sulzberg and Cotter (17). Purification of IV was made by dissolving it in a 5% $NaHCO_3$ solution in water, filtering and then precipitating with HCl. The purified product was transformed into the corresponding acid chloride (V) by reflux with excess thyonyl chloride, according to Kuder et al. (18). *2'-ethylacryl-4,5,7-trinitro-9-fluorenone-2-carboxylate.* To a solution of 25 g (0.0662 mole) 4,5,7-trinitro-9-fluorenone-2-carboxylic acid chloride in 250 ml tetrahydrofuran (THF), 9.23 ml (0.0662 mole) triethylamine dissolved in 30 ml THF were added dropwise under vigorous stirring. Then, 9.2 g (0.079 mole) hydroxyethylacrylate dissolved in 100 ml THF were added. During the addition, the hydrochloric triethylamine precipitated. After 2 hours stirring at room temperature, NEt_3.HCl was filtered and the solution was evaporated below 40°C on a rotovapor. The obtained solid was dissolved in chloroform and the solution washed with 5% $NaHCO_3$ solution in water, water, and finally dried on $CaCl_2$. The same solution was chromatographied on a coloumn with carbo animalis ($CHCl_3$ eluent), then it was concentrated to less than 5% in $CHCl_3$ and precipitated in petroleum ether. The white-yellow product was filtered, dried and reprecipitated with petroleum ether from 5% solution in chloroform, affording 22.7 g (75%) white-yellow powder. Repeated attempts to recrystallize the final product from different solvents or solvent mixtures failed. Other trinitrofluorenone or trinitrofluorene monomers (14,16,19,20) also could not be recrystallized. IR(KBr) : 1720 ($\nu C=O$), 1600 ($\nu C=C$), 1530 (νNO_2 asym.), 1340 cm^{-1}(νNO_2 sym.). NMR($CDCl_3$) : 4.62 (CH_2CH_2), 5.8-6.7 ($CH=CH_2$), 8.6-8.8 ($H_{1,3,8}$ aromatic), 8.9 ppm (H_6 aromatic). Elemental analysis corresponds to the theoretical one.

Copolymerizations were performed in dioxane solutions under argon at 60°C in sealed ampoules. The total concentration of monomers was 0.5 mole/l and the initiator (AIBN) was 1% from monomers. The copolymers were precipitated with methanol and purified by reprecipitation with methanol from THF solutions. ETNFA homopolymerization, performed in the same conditions, gave 6.21 % poly(ETNFA) in 31.5 hours.

^1H-NMR spectra were registered on a JEOL C-60HL spectrometer in $DMSOd_6$ solutions at different temperatures.

RESULTS AND DISCUSSION

The obtained copolymers are brown-violet colored and soluble in dioxane, THF, DMSO, DMF, especially at high temperatures. The increase of color intensity and the decrease of the solubility are directly connected with the increase of alternating sequences.

Figure 1 represents the ^1H-NMR spectrum of sample 4A together with signal assignments. Copolymer compositions were determined from the aromatic : CH_2CH_2 signal integral ratio. The copolymerization data are presented in table 1.

TABLE 1.
Copolymerization data

Sample	$x = [M_1]/[M_2]$	Time (h)	Conversion (%)	$y = d[M_1]/d[M_2]$
1A	7.00	20.00	1.85	6.69
2A	3.00	23.50	5.04	3.00
3A	1.67	27.58	5.17	1.94
4A	1.00	28.58	6.50	1.22
5A	0.60	28.67	5.77	0.82
6A	0.33	28.67	5.47	0.47
7A	0.14	29.42	4.80	0.20

The copolymerization diagram is presented in figure 2, and data processing with Kelen-Tüdös equation (figure 3)gives the results :

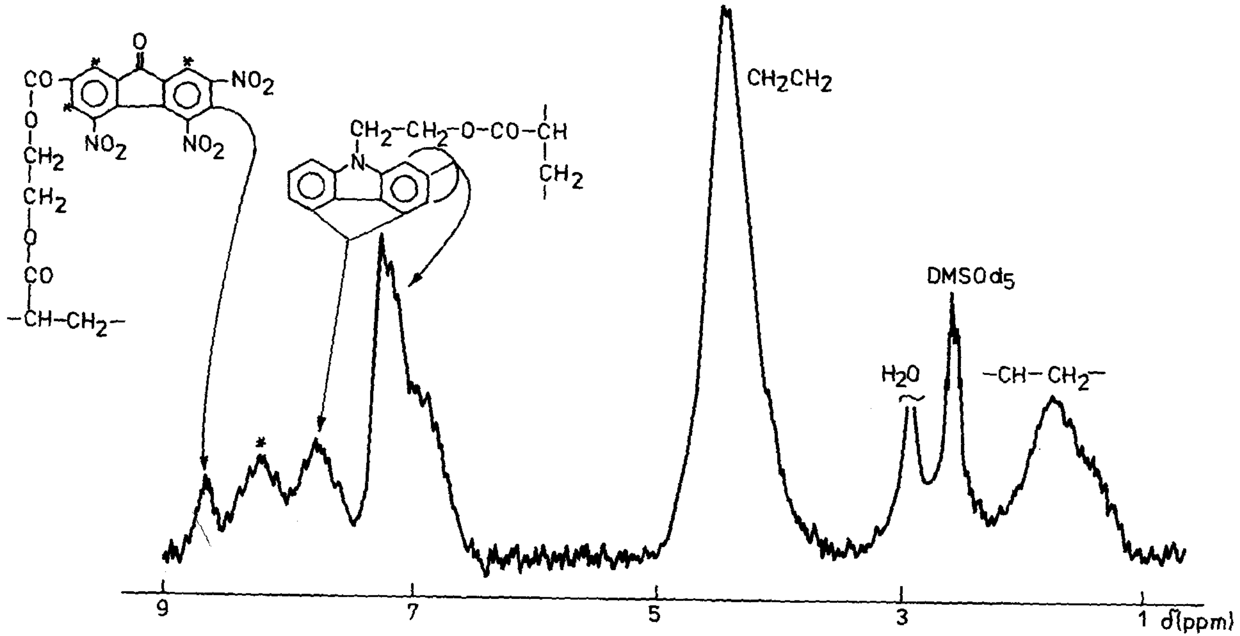

Figure 1. ^{1}H-NMR spectrum of sample 4A

$r_1 = 0.85 \pm 0.11 \quad r_2 = 0.54 \pm 0.10$

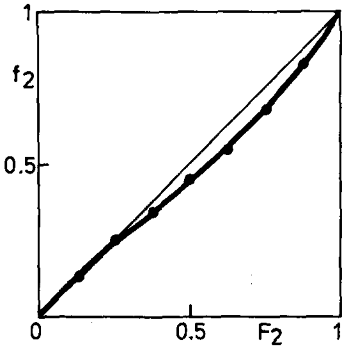

Figure 2. Copolymerization diagram

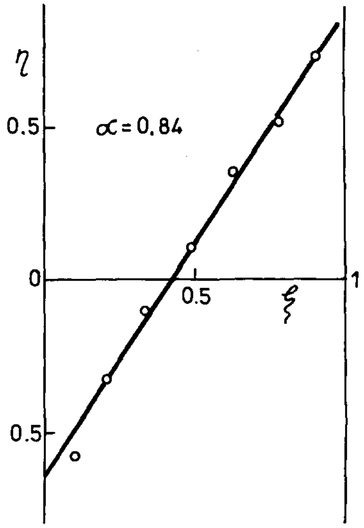

Figure 3. Kelen-Tüdös plot

The error was determined for 95% confidence interval, according to Kelen, Tüdös and Turcsanyi (21). Although the error seem to be rather high, the terminal model validity is verified by the relation :

$$\xi^{\square} = \frac{|\Delta r_1 \, \Delta r_2|}{r_1 r_2} = 0.02 < 0.1 \quad (22).$$

Consequently, this system can be correctly approximated by a simple terminal model of copolymerization. It seems that, when both comonomers can homopolymerize, the simple terminal mechanism has to be taken into account (6,8-10). The intermonomeric CTC participation is important only when at least one of the monomers does not homopolymerize (2-5,7).

Intramolecular complexation is evidenced by measuring the chemical shift of the 6th aromatic proton of ETNFA structural unit (the most deshielded). In poly(ETNFA) this chemical shift is 8.80 ppm from TMS. The high-field shift of this signal in copolymer spectra is the proof of the intramolecular complexation (1-13). Figure 4 represents this chemical shift against the ETNFA structural units being in alternating sequences

($\frac{1}{2}f_{12}/f_2$). At 25 and 80°C, the same straight line is obtained. At 150°C, the lower slope of the straight line indicates a decomplexation due to the increased segmental mobility given by the temperature.

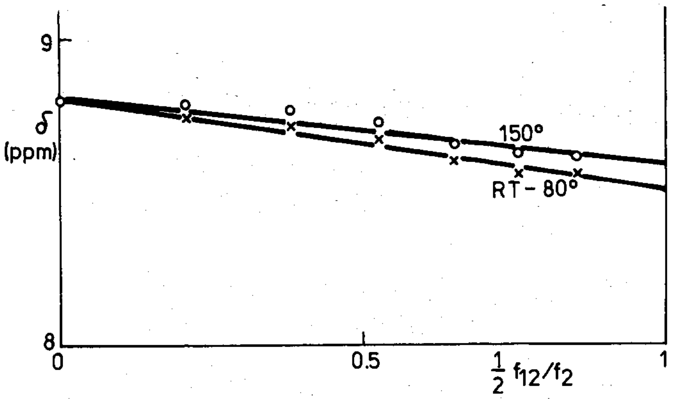

Figure 4. Chemical shift of 6th aromatic proton of ETNFA structural unit against ETNFA unit fraction being in alternating sequences

CONCLUSIONS

Radical copolymerization of HECA and ETNFA gives statistic copolymers, according to the simple terminal mechanism. The obtained copolymers are strong intramolecular CTC, because a rather high temperature (150°C) is required for partial decomplexation. At 80°C, no decomplexation can be seen.

Detailed results on intramolecular complexation and on electrical properties of these copolymers will be reported in the near future.

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