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Intramolecular Charge Transfer Complexes

15. Copolymers of N-(2-hydroxyethyl)Carbazolyl Methacrylate with 2'-Ethylacryl- and 2'-Ethylmethacryl-4,5,7-Trinitro-9-Fluorenon-2-Carboxylate

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Dedicated to Prof. G. B. Butler on the occasion of his 65th anniversary

SUMMARY

Radical copolymerization of N-(2-hydroxyethyl)carbazolyl methacrylate (HECM, M_1) with 2'-ethylacryl-(ETNFA) and 2'-ethylmethacryl-(ETNFM)-4,5,7-trinitro-9-fluorenon-2-carboxylate (M_2), respectively, can be approximated by the simple terminal model having the parameters :

HECM-ETNFM	$r_1 = 0.66$	$r_2 = 0.40$
HECM-ETNFA	$r_1 = 0.84$	$r_2 = 0.10$

Two intramolecular charge transfer complexes copolymers are obtained. Analysis of intramolecular complexation suggests a more complicated copolymerization mechanism, especially in the case of HECM-ETNFA system. Also, the complexation seems to be independent on the acrylate or methacrylate type of the comonomers.

INTRODUCTION

In a previous paper (SIMIONESCU et al. 1980a) the synthesis of an intramolecular charge transfer complex (CTC) copolymer having carbazole and 4,5,7-trinitro-9-fluorenone as side groups of structural units was presented. It was obtained by N-(2-hydroxyethyl)carbazolyl acrylate and 2'-ethylacryl-4,5,7-trinitro-9-fluorenon-2-carboxylate (ETNFA) copolymerization.

One of the factors which can affect the intramolecular complexation is the α-substitution at the comonomers double bond (PERCEC et al. 1980). With monomers having a small distance between the acceptor group and the double bond (e.g. 2,4-dinitrophenyl acrylate and methacrylate (SIMIONESCU et al. 1980b)), this is a decisive factor for intramolecular complexation. Increasing this distance, the copolymer configuration (which depends on the α-substitution of the double bond (SIMIONESCU et al. 1980c)) becomes less important, because the complexation can be realized even in cosyndiotactic alternating diads (SIMIONESCU et al. 1980c,d).

ETNFA is a monomer with a relatively large distance between the complexing group and the double bond. This paper presents the synthesis of two other intramolecular CTC from carbazole and trinitrofluorenone-containing acrylates and methacrylates, in order to observe the dependence of intramole-

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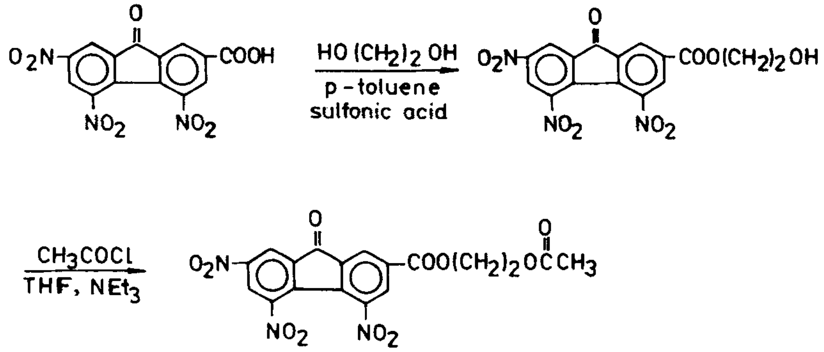
cular complexation on the chain configuration.

EXPERIMENTAL

The donor monomer was N-(2-hydroxyethyl)carbazolyl methacrylate (HECM, M_1) synthesized as previously described (SIMIONESCU et al. 1980e). Acceptor monomers (M_2) were ETNFA (SIMIONESCU et al. 1980a) and 2'-ethylmethacryl-4,5,7-trinitro-9-fluorenon-2-carboxylate (ETNFM), synthesized according to TURNER (1980) and realizing purifications described for ETNFA (SIMIONESCU et al. 1980a).

The donor homopolymer model : N-(2-hydroxyethyl)carbazolyl acetate (HECAc) was synthesized as described (SIMIONESCU and PERCEC 1980). The acceptor homopolymer model : 2'-ethylacetyl-4,5,7-trinitro-9-fluorenon-2-carboxylate (ETNFAc) was synthesized according to the scheme :



2'-hydroxyethyl-4,5,7-trinitro-9-fluorenon-2-carboxylate

A mixture of 40 g (0.11 moles) of 4,5,7-trinitro-9-fluorenon-2-carboxylic acid (SIMIONESCU et al. 1980a), 300 ml ethyleneglycol and 4 g p-toluene sulfonic acid was heated under stirring during 8 hours at 110°C. After cooling, the ethyleneglycol solution was precipitated in water and the ethyleneglycol insoluble part was extracted with hot acetone and precipitated in water. The precipitate was dried and recrystallized from acetone, yielding 35 g (79.1%) yellow crystals. m.p. 97-98°C. IR (KBr) : 3340 cm^{-1}(ν OH), 1710, 1730 cm^{-1} (ν C=O), 1535 cm^{-1} (ν NO$_2$ asym.), 1340 cm^{-1} (ν NO$_2$ sym.). NMR (acetone-d$_6$, 50°C): 8.83 ppm (6th aromatic proton), 8.63 ppm (3rd and 8th aromatic protons), 8.50 ppm (1st aromatic proton), J meta = 2 Hz, 4.46 ppm (-CH$_2$OCO-), 3.85 ppm (-CH$_2$O-) J-CH$_2$CH$_2$ = 5.5 Hz.

2'-ethylacetyl-4,5,7-trinitro-9-fluorenon-2-carboxylate

To a solution of 8 g (0.02 moles) 2'-hydroxyethyl-4,5,7-trinitro-9-fluorenon-2-carboxylate, 150 ml tetrahydrofuran (THF) and 3.6 ml (0.026 moles) triethylamine cooled at 10°C and strongly stirred, a mixture of 1.85 ml (0.026 moles) acetyl chloride and 5 ml THF was added dropwise. After 8 hours of reaction at room temperature, NEt$_3$.HCl was filtered and the solution evaporated at 40°C. The solid product was dissloved in $CHCl_3$ and washed with water, the solution was dried on $CaCl_2$ and precipitated with petroleum ether. 7.6 g (85%) yellow powder was obtained. m.p. = 87-88°C. IR(KBr) : 1730 cm^{-1} (ν C=O), 1535 cm^{-1} (ν NO_2 asym.), 1340 cm^{-1} (ν NO_2 sym.). NMR ($DMSOd_6$, RT) : 8.94 ppm (6th aromatic proton), 8.75 ppm (3rd aromatic proton), 8.68 ppm (8th aromatic proton), 8.48 ppm (1st aromatic proton), J meta = 2 Hz, 4.55 ppm ($-CH_2CH_2-$), 2.04 ppm (CH_3CO).

Copolymerizations were carried out in sealed ampoules, at 60°C, in solutions 0.5M in dioxane, under argon, with 1% AIBN from monomers. The copolymerization data are presented in table 1.

TABLE 1.
Copolymerization data

HECM-ETNFM					HECM-ETNFA				
Sample	x	Time (h)	Conv. (%)	y	Sample	x	Time (h)	Conv. (%)	y
1M	7.00	13.6	34.8	5.25	8A	7.00	19.3	54.3	6.14
2M	3.00	13.6	26.6	2.70	9A	3.00	19.5	53.7	3.17
3M	1.67	13.7	32.4	1.70	10A	1.67	19.6	30.3	2.23
4M	1.00	13.7	26.4	1.17	11A	1.00	19.7	21.1	1.63
5M	0.60	13.8	27.7	0.79	12A	0.60	19.8	20.3	1.22
6M	0.33	13.8	25.9	0.52	13A	0.33	19.8	10.3	0.85
7M	0.14	13.9	18.6	0.27	14A	0.14	19.9	6.3	0.61
poly(ETNFM)		61.5	10.4	-	poly(ETNFA)		31.5	6.2	-

$x = [M_1]/[M_2]$; $y = d[M_1]/d[M_2]$

Copolymer composition was determined from the ^1H-NMR spectra registered in $DMFd_7$ solutions on a JEOL C-60HL spectrometer. Electronic absorption spectra were registered on a Unicam SP 800 spectrophotometer in THF solutions.

RESULTS AND DISCUSSIONS

Copolymerization diagrams are presented in figure 1.

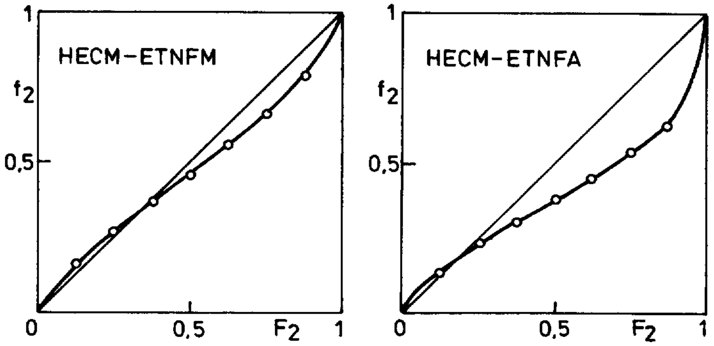


Figure 1. Copolymerization diagrams

As it can be seen, ETNFM is more reactive than ETNFA. Data processing, according to TUDOS et al. (1976), gives the plots presented in figure 2, and the relative reactivity values :

HECM-ETNFM	$r_1 = 0.66$	$r_2 = 0.40$
HECM-ETNFA	$r_1 = 0.84$	$r_2 = 0.10$

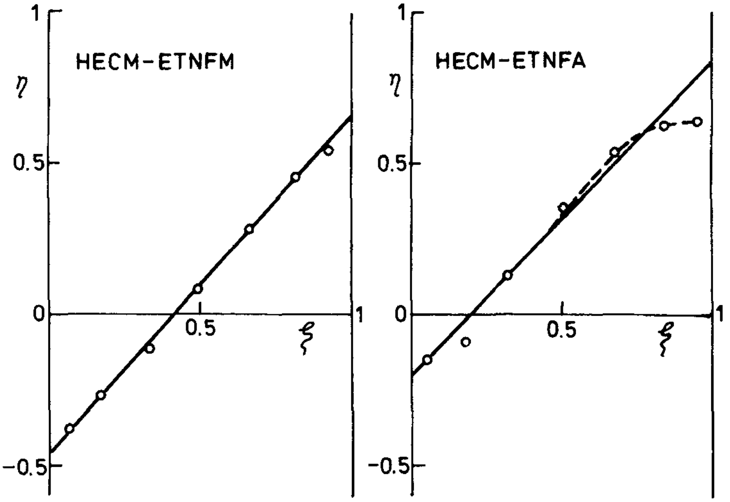


Figure 2. Kelen-Tüdös plots

The plots in figure 2 can be approximated by straight lines (terminal model of copolymerization), but for HECM-ETNFA system a slight curvature is observed. Diad sequence fraction calculation is made using the above reactivity ratio values, although from table 1 it can be seen that copolymerization rate is higher than the acceptor monomer homopolymerization rates. This suggests a copolymerization mechanism implying intermonomeric CTC participation (PERCEC et al. 1981a).

The copolymers are dark-violet colored and are soluble in THF, DMF and DMSO. The solubility is decreased at nearly 1:1 compositions, when solutions are obtained only at high temperatures.

The electronic absorption spectra of CTC between the model compounds (HECAc and ETNFAc) present two maxima corresponding to the transitions from the last and, respectively, penultimate occupied molecular orbital of the donor to the first free molecular orbital of the acceptor, located at $\lambda_1 = 565$ nm and $\lambda_2 = 460$ nm. These transitions correspond to those of CTCs : poly(N-vinyl carbazole)-2,4,7-trinitro-9-fluorenone and N-ethyl carbazole-2,4,7-trinitro-9-fluorenone (SIMIONESCU and PERCEC, 1979). The copolymers present a maximum at 460 nm and then a continuous absorption up to 800 nm, due to the configurational polydispersity. CTC of HECAc and ETNFAc absorbs up to 750 nm.

The intramolecular complexation degree is estimated measuring the chemical shift of the 6th aromatic proton from the acceptor structural unit (the most deshielded) as a function of the acceptor structural units fraction being in alternating sequences. In poly(ETNFM) and poly(ETNFA) this proton resonates at 6.1 ppm from the DMF signal. Figure 3 gives this dependence for spectra registered at 150°C.

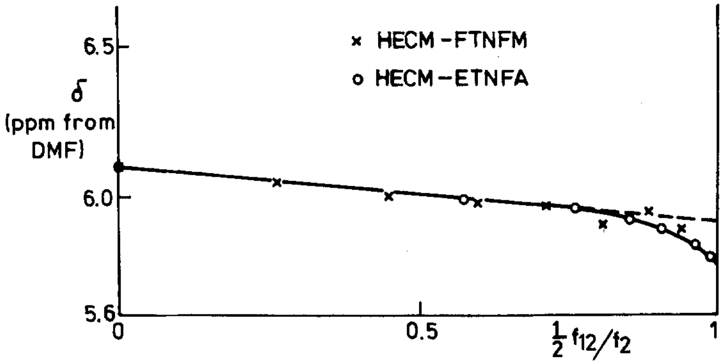


Figure 3. Chemical shift of the 6th aromatic proton from acceptor structural unit against $\frac{1}{2}f_{12}/f_2$

For poly(HECM-co-ETNFM) the points can be situated on a straight line, but for poly(HECM-co-ETNFA) the deviation from the straight line is obvious. Such curvatures were observed also for copolymers obtained with acryloyl-β-hydroxyethyl-3,5-dinitrobenzoate as acceptor monomer (PERCEC et al. 1981a,b, SIMIONESCU et al., submitted), which, as ETNFA, has low r_2 values. The explanation can be the unconcordance between the calculated sequence distribution (using the terminal model) and the real sequence distribution, given by the copolymerization model implying intermonomeric CTC participation.

Such anomalies make impossible at this moment the study of chain configuration influence on intramolecular complexation.

The intramolecular complexation dependence on spectrum registration temperature is given in figure 4. As for the precedent copolymer (SIMIONESCU et al. 1980a), the chemical shifts do not significantly change between 25 and ca. 100°C. The complexation is weaker at 150°C.

CONCLUSIONS

Two new intramolecular CTC copolymers are obtained, presenting intramolecular complexation even at high temperatures. The difference in the 6th aromatic proton of the acceptor unit chemical shift between the uncomplexed and the most complexed states is of 0.2 - 0.3 ppm, depending on system and on registration temperature. Consequently, they are rather strong CTC.

No essential difference can be seen between the copolymers proceeding from acrylate and methacrylate monomers. Therefore, here also, the rather large distance between the acceptor group and the main chain favours the complexation, independent on configuration.

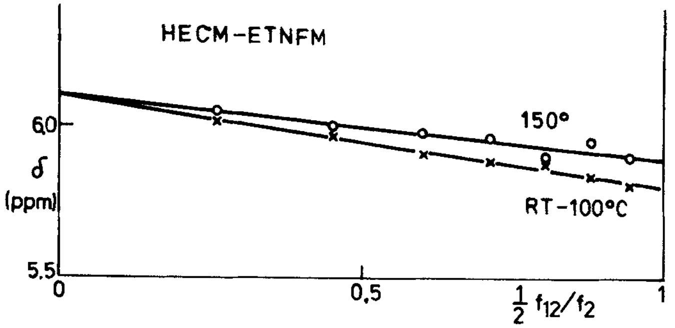


Figure 4. Chemical shift (ppm from DMF) of the 6th aromatic proton from ETNFM structural units against $\frac{1}{2}f_{12}/f_2$

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