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Intramolecular Charge Transfer Complexes

19. Copolymers Having as Acceptor Structural Units 3,5-dinitrobenzoic Acid Derivatives with Different Distances from the Main Chain

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SUMMARY

Increasing the distance between the acceptor group and the double bond for a series of monomers based on 3,5-dinitrobenzoic acid, the homopolymerization tendency is decreased. This permits the evidence of complex participation in copolymerization with the donor monomer N-(2-hydroxyethyl)carbazolyl methacrylate. The intramolecular complexation degree depends on the distance between the complexing group and the main chain and also on the side chain flexibility.

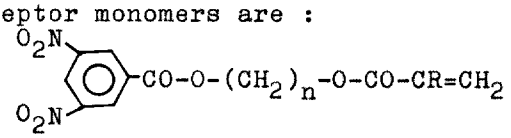
INTRODUCTION

In a precedent paper (SIMIONESCU et al. 1980a) we demonstrated that, incresing the distance between the complexing side group and the main chain, the intramolecular complexation can be realized even in unfavourable configurations, due to the increase of the complexing group mobility. Also, it was demonstrated that, although apparently the methacryloyl-(DNBM) and acryloyl-(DNBA) β-hydroxyethyl-3,5-dinitrobenzoate copolymerizations can be treated by the terminal model (the Kelen-Tüdös plots are straight lines), they belong to the charge transfer mechanism (PERCEC et al. 1981a and b, SIMIONESCU et al., submitted).

This paper presents the synthesis of four new monomers based on 3,5-dinitrobenzoic acid, having higher distances between the complexing group and the double bond, in order to study the importance of this distance for the copolymerization mechanism (donor monomer : N-(2-hydroxyethyl)carbazolyl methacrylate (HECM, M_1)) and for the intramolecular complexation.

EXPERIMENTAL

The acceptor monomers are :



	R = H	R = CH_3
n = 3	DNBPA	DNBPM
n = 4	DNBBA	DNBBM

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3-hydroxypropyl-3,5-dinitrobenzoate (DNBPH)

A mixture of 30 g (0.14 moles) 3,5-dinitrobenzoic acid, 0.8 g p-toluenesulfonic acid and 100 ml 1,3-propanediol was stirred 9 hours at 110°C. After cooling, a white product crystallized. A sufficient quantity of distilled water was added to separate all the reaction product from solution. Then the product was filtered and dried. After recrystallization from methanol 29.5 g (77.3%) white crystals with m.p. 63-64°C are obtained. IR (KBr) : 1712 cm^{-1} (ν C=O), 1535 cm^{-1} (ν NO_2 assym), 1341 cm^{-1}(ν NO_2 sym). NMR ($DMSOd_6$): 8.88 ppm (4th aromatic proton), 8.77 ppm (2nd and 6th aromatic protons), 4.42 ppm (triplet) and 3.54 ppm (triplet)(CH_2), 1.93 ppm (quintet)(CCH_2C).

4-hydroxybutyl-3,5-dinitrobenzoate (DNBBH)

It was synthesized like the precedent product. From 50 g (0.236 moles) 3,5-dinitrobenzoic acid, 2 g p-toluenesulfonic acid and 220 ml 1,4-butandiol, 43 g (63.5%) white crystals with m.p. 96-97°C were obtained. IR (KBr) : 1718 cm^{-1} (ν C=O), 1530 cm^{-1} (ν NO_2 asym), 1341 cm^{-1} (ν NO_2 sym). NMR ($DMSOd_6$): 8.9 ppm (4th aromatic proton), 8.77 ppm (2nd and 6th aromatic protons), 4.38 ppm (triplet) and 3.43 ppm (triplet) (CH_2), 1.71 ppm (multiplet, CCH_2CH_2C).

Methacryloyl-3-hydroxypropyl-3,5-dinitrobenzoate (DNBPM)

A mixture of 7.63 g (0.073 moles) methacryloyl chloride and 10 ml tetrahydrofuran (THF) dried on Na was added dropwise during 20 minutes under strong stirring to a solution of 15 g (0.056 moles) DNBPH and 10.22 ml (0.073 moles) triethylamine (TEA) in 75 ml THF (cooled at 6°C). The mixture was stirred one hour at 6°C and 6 hours at room temperature, then NEt_3.HCl was filtered, washed with THF and the solution concentrated on a rotovapour at ca. 35 ml below 35°C. The solution was poured into water and the oil layer extracted with ethylic ether, washed with $NaHCO_3$ aqueous solution, water, dried on $CaCl_2$ sicc. and finally chromatographied on alumine (ethylic ether eluent). Solvent evaporation below 30°C gave 14.21 g (75%) oleum product. IR (KBr) : 1700 cm^{-1} (ν C=O), 1615 cm^{-1} (ν C=C), 1522 cm^{-1} (ν NO_2 assym), 1332 cm^{-1} (ν NO_2 sym). NMR ($CDCl_3$): 8.98 ppm (aromatic), 5.50 and 6.00 ppm ($=CH_2$), 4.53 ppm (triplet), 4.30 ppm (triplet) and 2.25 ppm (quintet)(CH_2), 1.97 ppm (CH_3).

Acryloyl-3-hydroxypropyl-3,5-dinitrobenzoate (DNBPA)

It was synthesized like DNBPM. From 14 g (0.052 moles) DNBPH, 5.34 g (0.068 moles) acryloyl chloride, 9.52 ml (0.068 moles) TEA in 75 ml THF, 10.12 g (60%) of viscous liquid were obtained. IR (KBr) : 1710 cm^{-1} (ν C=O), 1612 cm^{-1} (ν C=C), 1525 cm^{-1} (ν NO_2 assym), 1335 cm^{-1} (ν NO_2 sym). NMR ($CDCl_3$) : 8.97 ppm (aromatic), 5.6-6.6 ppm ($CH=CH_2$), 4.1-4.7 ppm (multiplet) and 2.26 ppm (quintet)(CH_2).

Methacryloyl-4-hydroxybutyl-3,5-dinitrobenzoate (DNBBM)

It was synthesized like DNBPM. From 18 g (0.063 moles) DNBBH, 8.6 g (0.082 moles) methacryloyl chloride and 11.48 ml (0.082 moles) TEA in 75 ml THF, 16.2 g (73%) white crystals were obtained after recrystallization from methanol. m.p. 46-47°C. IR (KBr) : 1705 cm^{-1} (ν C=O), 1616 cm^{-1} (ν C=C), 1525 cm^{-1} (ν NO_2 assym), 1338 cm^{-1} (ν NO_2 sym). NMR ($CDCl_3$): 8.95 ppm (aromatic), 5.50 and 6.00 ppm ($=CH_2$), 4.50 ppm (triplet) and 4.20 ppm (triplet) (CH_2), 1.93 ppm (multiplet,

$CCH_2CH_2C + CH_3$).

Acryloyl-4-hydroxyethyl-3,5-dinitrobenzoate (DNBBA)

As for DNBBM, from 17 g (0.060 moles) DNBBH, 7.06 g (0.078 moles) acryloyl chloride and 10.92 ml (0.078 moles) TEA in 75 ml THF, 12.18 g (60%) white crystals (m.p. 42-43°C) were obtained after recrystallization from methanol. IR (KBr): 1710 cm^{-1} (ν C=O), 1615 cm^{-1} (ν C=C), 1535 cm^{-1} (ν NO_2 assym), 1338 cm^{-1} (ν NO_2 sym). NMR ($CDCl_3$) : 8.98 ppm (aromatic), 5.6-6.6 ppm ($CH=CH_2$), 4.50 ppm (triplet), 4.23 ppm (triplet) and 1.96 ppm (quintet)(CH_2).

Copolymerizations were performed in solution in dioxan at 60°C under argon in sealed ampoules at a total monomer concentration of 0.5 M and 1% AIBN from monomers. Copolymers were separated by precipitation in methanol and purified by reprecipitation in methanol from THF solutions. Copolymerization data are presented in table 1.

TABLE 1.
Copolymerization data

x	Sample	HECM-DNBPM Time (h)	Conversion(%)	y	Sample	HECM-DNBPA Time (h)	Conversion(%)	y
7.00	1p	2.2	27.2	6.69	8p	3.1	24.5	15.67
3.00	2p	3.1	25.4	3.76	9p	3.1	27.1	9.00
1.67	3p	4.5	28.5	2.33	10p	11.4	30.4	4.56
1.00	4p	4.5	21.0	1.56	11p	13.5	21.4	2.57
0.60	5p	11.4	36.6	0.96	12p	16.0	10.0	1.50
0.33	6p	11.5	27.0	0.58	13p	17.8	2.2	0.89
0.14	7p	11.6	16.4	0.28	14p	35.1	7.8	0.41
poly(DNBPM)		70.3	50.8	-	poly(DNBPA)	72.0	traces[+]	-
x	Sample	HECM-DNBBM Time (h)	Conversion(%)	y	Sample	HECM-DNBBA Time (h)	Conversion(%)	y
7.00	1b	2.0	13.0	6.14	8b	14.5	85.9	5.25
3.00	2b	2.0	4.6	3.17	9b	14.6	55.3	4.26
1.67	3b	3.3	5.1	1.94	10b	14.6	27.2	3.35
1.00	4b	14.4	35.2	1.33	11b	15.0	14.2	2.45
0.60	5b	14.4	29.1	0.85	12b	15.1	7.0	1.70
0.33	6b	14.5	28.8	0.45	13b	18.9	17.1	1.13
0.14	7b	14.5	23.6	0.25	14b	23.0	5.0	0.64
poly(DNBBM)		69.5	22.9	-	poly(DNBBA)	72.0	traces[+]	-

[+]homopolymerization in the presence of an equimolecular quantity of N-ethylcarbazole. Without complexant, both DNBPA and DNBBA do not homopolymerize. $x = [M_1]/[M_2]$; $y = d[M_1]/d[M_2]$

Copolymer composition was determined from ^{1}H-NMR spectra registered in $DMSOd_6$ at 150°C on a Jeol C-60HL spectrometer.

RESULTS AND DISCUSSION

Copolymerization diagrams are presented in figure 1. The methacrylates are more reactive in copolymerization than the respective acrylates, but less reactive than the donor monomer - HECM. Although both DNBPA and DNBBA do not homopolymerize, there are samples with more than 50% acceptor structural units of this type. Because both monomers generate homo-

polymers in the presence of electrono-donor substances, one can conclude that the copolymerization mechanism implies in these cases too, as for DNBA (PERCEC et al. 1981a) the intermonomeric charge transfer complex (CTC) participation.

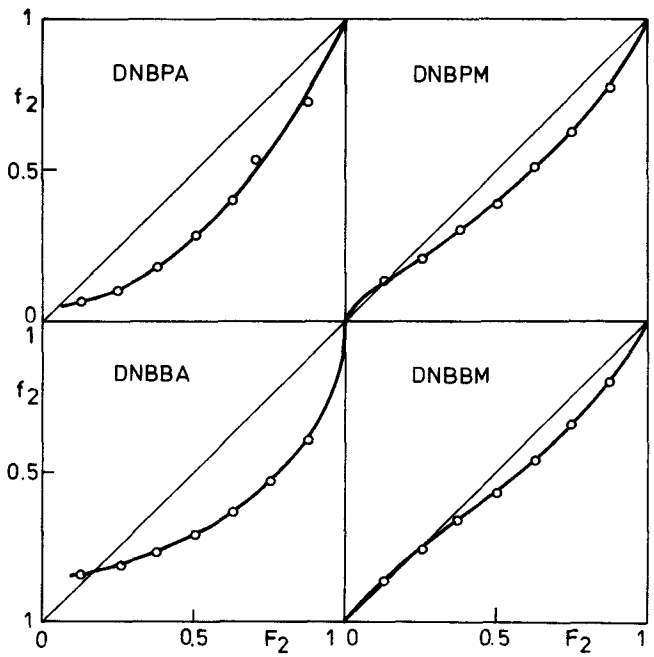

Figure 1. Copolymerization diagrams.

Copolymerization data processing according to TUDOS et al. (1976) gives the plots presented in figure 2. All plots are curves, clearly indicating the deviation from the terminal model of copolymerization. Therefore, increasing the distance between the complexing group and the monomer double bond, the role of the intermonomeric CTC in copolymerization seems to increase, its effect can no more be overlapped, as for DNBM and DNBA, when straight lines are obtained in the Kelen-Tüdös plots. The increase of the intermonomeric CTC participation is probably due to the decrease of the acceptor monomers homopolymerization tendency.

The intramolecular complexation degree is estimated measuring the chemical shift of the aromatic protons from acceptor structural units and plotting it against copolymer composition. The plot against calculated diad fraction has no physical significance, because these fractions should be experimentally determined. Figure 3 represents this chemical shift for HECM copolymers with DNBM (SIMIONESCU et al. 1980b), DNBPM and DNBBM. According to figure 3, poly(HECM-co-DNBBM) is a complex stronger than poly(HECM-co-DNBM), but weaker than poly(HECM-co-DNBPM). The conclusion is that, increasing the distance between the complexing side group and the main chain its mobility is increased and, therefore, it is more probable

to obtain a configuration which permits complexation.

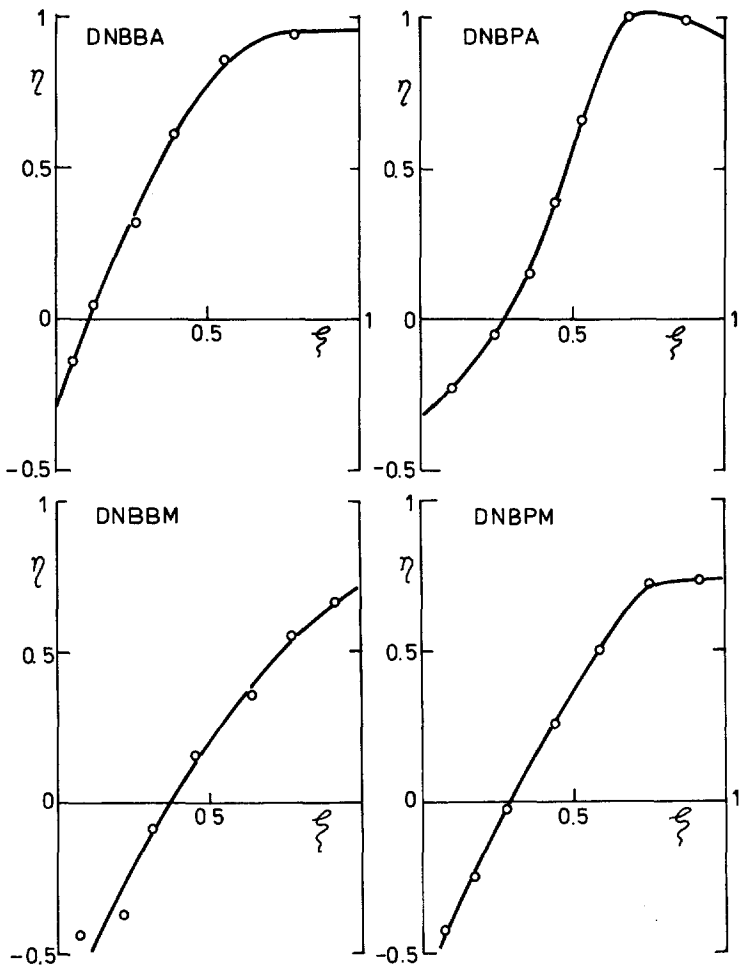

Figure 2. Kelen-Tüdös plots.

The stronger DNBPM complexes, as compared with DNBBM ones, are explained by the increased flexibility of DNBPM. The intramolecular complexation follows the lateral flexibility order, according to the melting points of the monomers and the intermediate hydroxy compounds (table 2).

The attempt to compare poly(HECM-co-DNBA) (PERCEC et al. 1981a) with poly(HECM-co-DNBPA) and poly(HECM-co-DNBBA), given in figure 4, gives rather curves than straight lines. The most pronounced curvature is presented by DNBBA, considered here as the weakest complex. Because these acrylates

copolymerize according to a mechanism completely different from the terminal one, probably the sequence distribution is no more proportional with the copolymer composition, and this gives the curvature in the plots of figure 4. Therefore, the comparison of the intramolecular complexation cannot be done without sequence distribution data.

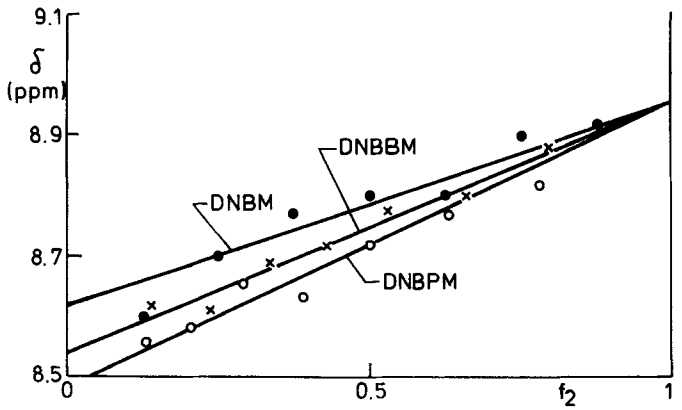

Figure 3. Chemical shift of acceptor structural units aromatic protons for poly(HECM-co-DNBM), poly(HECM-co-DNBPM) and poly(HECM-co-DNBBM).

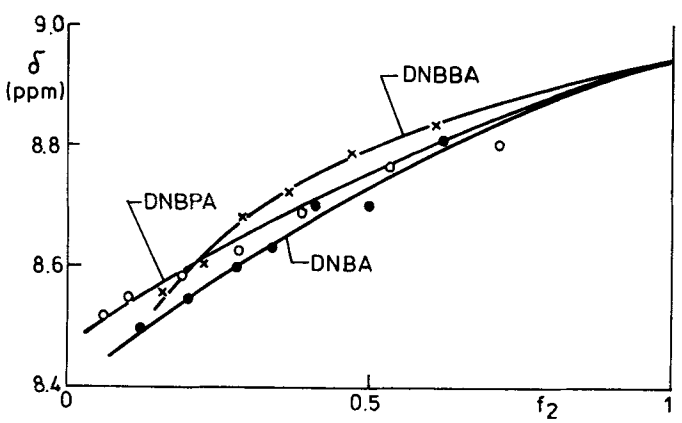

Figure 4. Chemical shift of acceptor structural units aromatic protons for poly(HECM-co-DNBA), poly(HECM-co-DNBPA) and poly(HECM-co-DNBBA).

TABLE 2.
Melting points (°C)

	hydroxy	acrylate	methacrylate
n = 2	138-139	61-62	65-66
n = 3	63-64	liquid	liquid
n = 4	96-97	42-43	46-47

CONCLUSIONS

The increase of the distance between the vinyl group and the electrono-acceptor substituent gives a decrease of the homopolymerization tendency of the corresponding monomers and, consequently, an increase of the intermonomeric CTC role in copolymerization. There is a competition between the distance separating the acceptor groups from the main chain and their flexibility in the obtaining of an optimum intramolecular complexation.

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