Intramolecular Charge Transfer Complexes

11. Configuration of Methacryloyl β-Hydroxyethyl-3,5-Dinitrobenzoate Copolymers with N-(2-Hydroxyethyl) Carbazolyl Acrylate and Methacrylate

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SUMMARY

The α-methyl signal in the ^{1}H-NMR spectra of methacryloyl β-hydroxyethyl-3,5-dinitrobenzoate (DNBM) copolymers with N-(2-hydroxyethyl)carbyzolyl acrylate (HECA) and methacrylate (HECM), respectively, is analysed in terms of sequence distribution and configuration. The coisotactic alternating addition probability has the values $\sigma = 0.2$ for poly(HECM-co-DNBM) and $\sigma = 0.7$ for poly(HECA-co-DNBM). Consequently, the same intramolecular complexation degree for both systems at the same sequence distribution, arises from the increased mobility of the side-groups.

INTRODUCTION

Of the factors which affect the microstructure of copolymers obtained from an electrono-donor and electrono-acceptor monomer pair, and which determine the intramolecular complexation degree, the α-substitution of the monomer double bond plays a very important part. With comonomers having the acceptor group directly connected with the double bond (picryl methacrylate, 2,4-dinitrophenyl methacrylate and acrylate), different intramolecular complexation degrees were obtained for the same sequence distribution (1-6), due to configurational differences. Ito et al. (7) supposed that with unsubstituted monomers, a preference for coisotactic configuration is obtained, if one of the monomers is α-substituted the configuration will be coheterotactic, and with both monomers α-substituted, the chain is more cosyndiotactic. This last case was demonstrated for many methacrylate pairs (8,9).

By increasing the distance between the acceptor group and the monomer double bond, similar complexation degrees were obtained in copolymers for the same sequence distribution, irrespective to the α-substitution of the monomer. This is the case of poly(N-(2-hydroxyethyl)carbazolyl acrylate (HECA)-co-methacryloyl β-hydroxyethyl-3,5-dinitrobenzoate (DNBM)) and poly(N-(2-hydroxyethyl)carbazolyl methacrylate (HECM)-co-DNBM)

(10). There are two possible explanations for this phenomenon :
- the configuration of the two copolymers is the same, or
- the increased distance between acceptor group and the main chain determines an increased mobility of the side-groups, and permits the intramolecular complexation independent on configuration, as was suggested on a steric model of an alternating cosyndiotactic diad (10, figure 4).
The aim of this paper is to determine the configurational parameters for poly(HECA-co-DNBM) and poly(HECM-co-DNBM) analysing the α-methyl signal in the ^{1}H-NMR spectra in order to find out the correct explanation.

EXPERIMENTAL

Monomer and copolymer synthesis were presented in the previous paper (10). The ^{1}H-NMR spectra were registered on a JEOL C-60HL spectrometer in DMSOd$_6$ solutions at 150°C. The relative intensities of the α-methyl signal parts were obtained by elemental curve deconvolution (11).

RESULTS AND DISCUSSION

Figure 1 presents the α-methyl region of the ^{1}H-NMR spectra of poly(HECM-co-DNBM). The signal is split in 6 parts having 0.18 ppm between them. The α-methyl region of poly(HECM) has three parts at 0.56, 0.38 and 0.20 ppm assigned to iso, hetero and syndiotactic triads, respectively. For poly(DNBM), there is also a three part splitting, centered at 1.10, 0.92 and 0.74 ppm, similary assigned. From the relative intensities of the three parts of the α-methyl signal, one can calculate the isotactic homoaddition probability for the two homopolymers, as follows :

poly(HECM)
$$\begin{cases} F_{0.56} = \sigma_{11}^2 \\ F_{0.38} = 2\sigma_{11}(1 - \sigma_{11}) \\ F_{0.20} = (1 - \sigma_{11})^2 \end{cases}$$

poly(DNBM)
$$\begin{cases} F_{1.10} = \sigma_{22}^2 \\ F_{0.92} = 2\sigma_{22}(1 - \sigma_{22}) \\ F_{0.74} = (1 - \sigma_{22})^2 \end{cases}$$

where F is the indexed part of the α-methyl signal fraction, and σ_{11} and σ_{22} are the configurational parameters of the homopolymers. The values obtained are :
$$\sigma_{11} = 0.21 \quad \sigma_{22} = 0.26$$
In the copolymer spectra, the assignment of the α-methyl signal can be made according to Klesper's hypo-
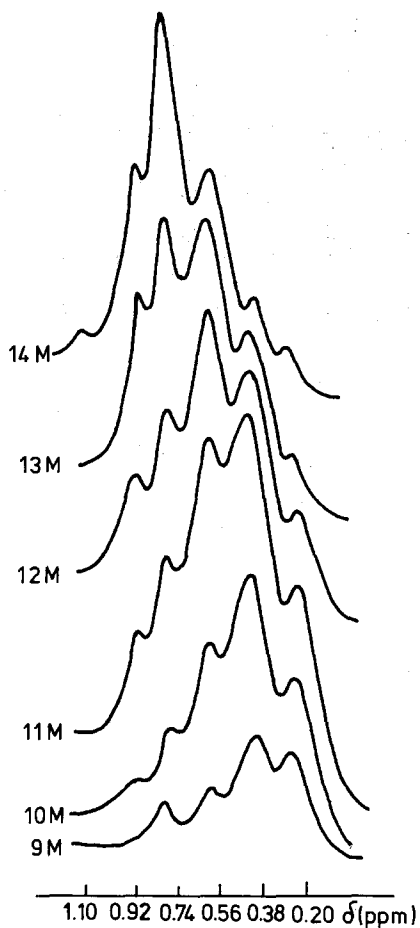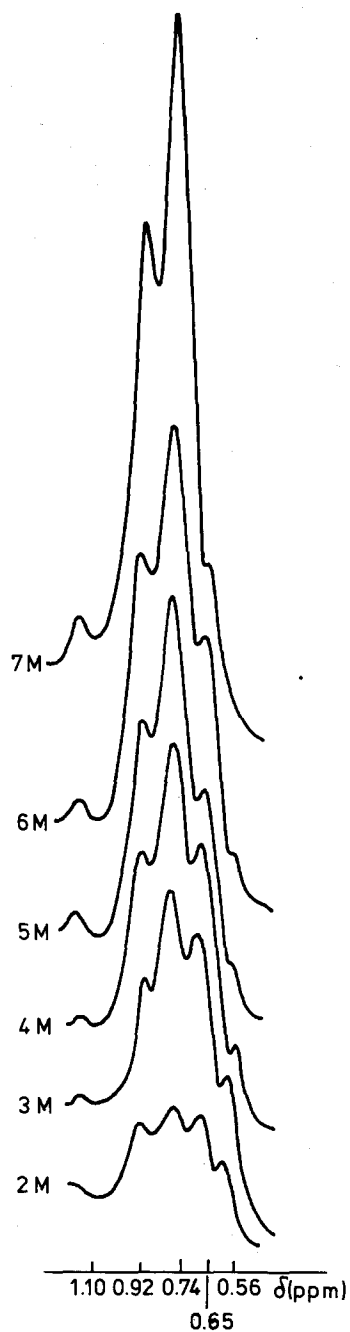
poly(HECM-co-DNBM)

poly(HECA-co-DNBM)

Figure 1. α-methyl signal in
poly(HECM-co-DNBM)

Figure 3. α-methyl signal in
poly(HECA-co-DNBM)

thesis (12) constructed for methyl methacrylate- me-
thacrylic acid copolymers, which is : the substitution
of a structural unit does not change the configuratio-
nal splitting. The same hypothesis was used by Harwood
(8) for methyl methacrylate- phenyl methacrylate copo-
lymers. Table 1 gives the signal assignment of poly
(HECM-co-DNBM).

TABLE 1.

α-CH$_3$ signal of poly(HECM-co-DNBM)

Chem. shift (ppm)	DNBM-centered triads			HECM-centered triads		
	s	h	i	s	h	i
1.10			222			
0.92		222	221			212
0.74	222	221	121		212	112
0.56	221	121		212	112	111
0.38	121			112	111	
0.20				111		

Here s = syndiotactic triad (s = rr, two racemic con-
figurations), h = heterotactic triad (h = mr or rm,
a meso and a racemic configuration), i = isotactic
triad (i = mm), 2 is DNBM and 1 is HECM.
According to table 1, the equations (1) are obtained :

$$F_{1.10} = \sigma_{22}^2 \, f_{222}$$

$$F_{0.92} = 2\sigma_{22}(1 - \sigma_{22})f_{222} + \sigma_{22}\sigma f_{221} + \sigma^2 f_{212}$$

$$F_{0.74} = (1 - \sigma_{22})^2 f_{222} + [\sigma_{22}(1 - \sigma) + \sigma(1 - \sigma_{22})]f_{221} +$$
$$+ \sigma^2 f_{121} + 2\sigma(1 - \sigma)f_{212} + \sigma_{11}\sigma f_{112}$$

$$F_{0.56} = (1 - \sigma_{22})(1 - \sigma)f_{221} + 2\sigma(1 - \sigma)f_{121} + \quad (1)$$
$$+ (1 - \sigma)^2 \, f_{212} + [\sigma_{11}(1 - \sigma) + \sigma(1 - \sigma_{11})]f_{112} +$$
$$+ \sigma_{11}^2 f_{111}$$

$$F_{0.38} = (1 - \sigma)^2 f_{121} + (1 - \sigma_{11})(1 - \sigma)f_{112} +$$
$$+ 2\sigma_{11}(1 - \sigma_{11})f_{111}$$

$$F_{0.20} = (1 - \sigma_{11})^2 f_{111}$$

where $f_{i..}$ is the fraction of i.. triad and σ is the
coisotactic alternating addition probability. Triad
fractions are calculated with the simple relations :

$f_{111} = f_1^3$, $f_{112} = 2f_1^2 f_2$, $f_{212} = f_1 f_2^2$, $f_{222} = f_2^3$,
$f_{221} = 2f_2^2 f_1$, $f_{121} = f_1^2 f_2$ which are valid for azeotro-
pic systems, as poly(HECM-co-DNBM) is (10).

The σ-value determination consists in finding the best concordance between calculated and experimental F, by replacing σ_{11} and σ_{22} in eqs.(1).
Figure 2 gives this concordance obtained for $\sigma = 0.2$.
Taking into account that the error of deconvolution of α-methyl signal is relatively high ($\pm 10\%$), the $\sigma = 0.2$ value can be considered with an approximation of ± 0.03
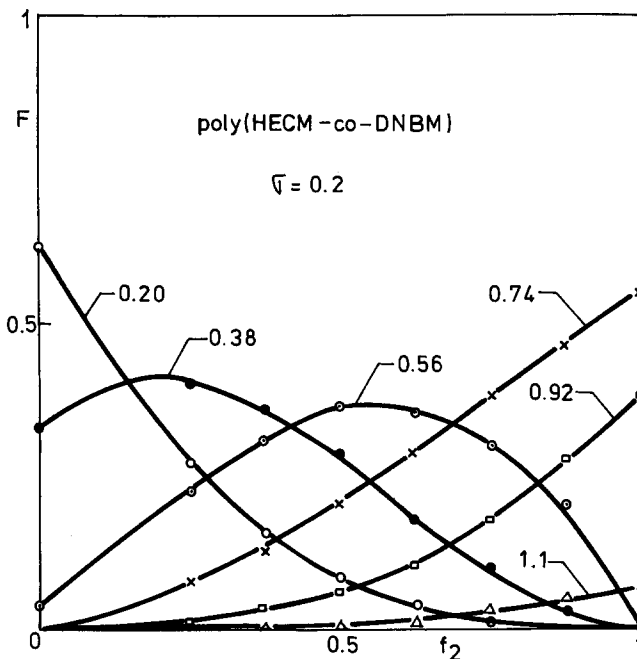

Figure 2. Experimental (points) and calculated (lines) α-methyl signal fractions ($\sigma = 0.2$) for poly(HECM-co-DNBM)

Figure 3 represents the α-methyl signal splitting for poly(HECA-co-DNBM). Besides the disappearance of the HECA-centered triads, there are also splitting differences, explained by the replacement of a methacrylic structural unit by an acrylic one. The α-methyl signal has 5 parts, the splitting between them being 0.18 ppm for the first three and 0.09 ppm for the last three. Table 2 gives the assignment of the α-methyl signal in poly(HECA-co-DNBM). The most important differences as compared with poly(HECM-co-DNBM) exist for the cosyndiotactic triads.
The equations (2) are derived from this assignment.

TABLE 2.
α-CH$_3$ signal of poly(HECA-co-DNBM)

Chemical shift (ppm)	DNBM-centered triads		
	i	h	s
1.10			222
0.92		222	221
0.74	222	2$_m$2$_r$1	121
0.65	221	2$_r$2$_m$1	
0.56	121	121	

$$F_{1.10} = \sigma_{22}^2 f_{222}$$

$$F_{0.92} = 2\sigma_{22}(1 - \sigma_{22})f_{222} + \sigma_{22}\sigma f_{221}$$

$$F_{0.74} = (1 - \sigma_{22})^2 f_{222} + \sigma_{22}(1 - \sigma)f_{221} + \sigma^2 f_{121} \quad (2)$$

$$F_{0.65} = (1 - \sigma_{22})f_{221}$$

$$F_{0.56} = (1 - \sigma^2)f_{121}$$

2-centered triad fractions are normalized to unity according to the relations :

$f_{222} = P_{22}^2$, $f_{221} = 2P_{21}P_{22}$, $f_{121} = P_{21}^2$ where

$P_{22} = (r_2/x)/(1 + (r_2/x))$ and $P_{21} = 1 - P_{22}$; r_2 and x are given in the preceeding paper (10).
Replacing σ_{22} in eqs.(2), the best concordance between calculated and experimental F is obtained with $\sigma = 0.7$, also with an $\pm$ 0.03 approximation (figure 4).
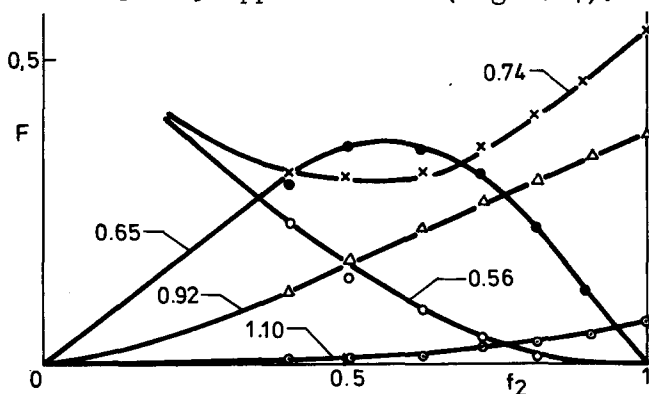

Figure 4. Experimental (points) and calculated (lines) α-methyl signal fractions ($\sigma = 0.7$) for poly(HECA-co-DNBM)

CONCLUSIONS

The σ-values found for the two systems are very different. In the methacrylate-methacrylate system there is a pronounced tendency to cosyndiotacticity, as in the most systems of this type (9), in the methacrylate-acrylate system there is, on the contrary, a tendency to coisotacticity ($\sigma_1 > 0.5$). The σ-value does not obey the rule $\sigma = (\sigma_{11} \sigma_{22})^2$, which means that not only the comonomer stericity determines the addition mode, but there are also other factors. For systems like these, presenting donor-acceptor interactions, this is an expected result.

Consequently, the sole explanation for the independence of the intramolecular complexation degree on copolymer configuration is the increase of side-group mobility and the possibility to realize the complexation even in cosyndiotactic configurations.

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