Polymer Bulletin 9, 67-74 (1983)

Polymer Bulletin

Comparison of Intramolecular Complexation in Several Charge Transfer Complexes Copolymers

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SUMMARY

Another representation of the chemical shift of the acceptor structural units' protons in the NMR spectra is proposed in order to make possible direct comparison between intramolecular complexation in intramolecular charge transfer complexes obtained by copolymerization. The influence of synthesis conditions and comonomer type on the intramolecular complexation is discussed.

INTRODUCTION

In a series of papers (PERCEC et al. 1981d), intramolecular charge transfer complexes were obtained by radical copolymerization of electrono-donor with electrono-acceptor monomers. The intramolecular charge transfer interaction was evidenced by the absorption in the electronic spectra and by ^{1}H-NMR. The NMR method was proved to be more effective, because in the electronic spectra the charge transfer bands were overlapped by the most intense bands characteristic to each chromophore. To compare different copolymers from the point of view of the intramolecular complexation, the chemical shift of the aromatic protons from the acceptor structural unit was measured and represented against copolymer composition (PERCEC et al. 1981a), or against diad fraction (PERCEC et al. 1981b). However, due to the complex mechanism of copolymerization, it was difficult to compare directly these representations which were sometimes straight lines and sometimes curves.

EXPERIMENTAL

The chemical shift of the aromatic protons from the acceptor structural units is an average of the uncomplexed and complexed states (figure 1).

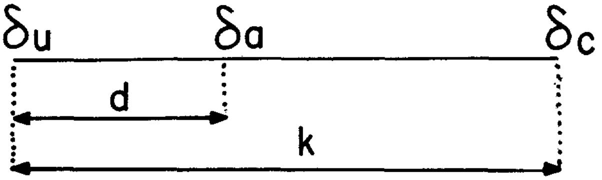

Figure 1. Chemical shift scheme

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The actual chemical shift can be written as :

$$\delta_a = \delta_u \frac{u}{u+c} + \delta_c \frac{c}{u+c} \qquad (1)$$

where : δ_a = the actual chemical shift

δ_u = the chemical shift of the same protons in the pure uncomplexed state

δ_c = the chemical shift in the pure complexed state

u = concentration of uncomplexed structural units

c = concentration of complexed structural units.

Such a relation was described by TSUCHIDA et al. (1972) for micromolecular complexes. In the case of intramacromolecular complexes, δ_u can be measured in the ^{1}H-NMR spectrum of the homopolymer having only acceptor structural units, registered in the same solvent as the copolymers, δ_a is measured in each copolymer spectrum and the sum u + c = f_2 is the fraction of the acceptor structural unit in the copolymers. δ_c, u and c are unknown.
One can rewrite eq. (1) as :

$$f_2 \delta_a = u \delta_u + c \delta_c$$

and, then,

$$kc = f_2 d \qquad (2)$$

where d and k are shown in figure 1.
In eq. (2), f_2 is known for each sample, d is measured for each sample, and their product represented against f_2 gives the effective intramolecular complex concentration (c) multiplied by a constant (k).

RESULTS AND DISCUSSION

This method was applied for the whole series of intramolecular complexes previously reported. One can directly compare only complexes having the same δ_c, i.e. the same complexing groups. The most studied systems were obtained from monomers having N-(2-hydroxyethyl)carbazole as donor and 3,5-dinitrobenzoate derivatives as acceptor (SIMIONESCU et al. 1980a,1981a; PERCEC et al. 1981c).
Poly(N-(2-hydroxyethyl)carbazolyl methacrylate (HECM)-co-methacryloyl-2'-hydroxyethyl-3,5-dinitrobenzoate (DNBM)) was obtained in different solvents and at different temperatures (PERCEC et al. 1981c). Figure 2 compares the intramolecular complexation for poly(HECM-co-DNBM) obtained at different temperatures.
It is to be noted that k has the dimensions of a chemical shift (see figure 1) whereas c is dimensionless (it is a molar fraction). The actual value of the kc product has no physical significance and can be expressed either in Hz or in ppm. Therefore, all the following figures have no units for the kc product, and the comparison between the maxima is made taking the smallest one as a reference (see table 1).
Successful attempts to measure δ_c would permit direct c determination. The temperature interval in figure 2 is not very high, but a difference can be seen, mainly between 100°C and the other two tempertures. The intramolecular complexation is lower when the *copolymer is synthesized* at higher temperature, because dissociation phenomena of the intermonomeric complex are more probable.

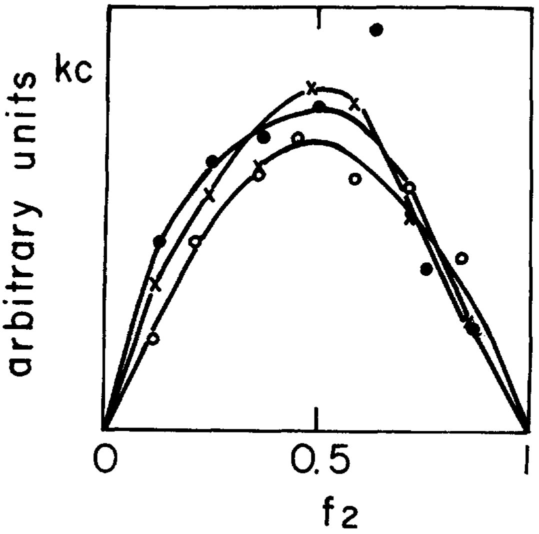


Figure 2. Intramolecular complex concentration for poly(HECM-co-DNBM) obtained at :

- ● 60°C
- x 80°C
- o 100°C

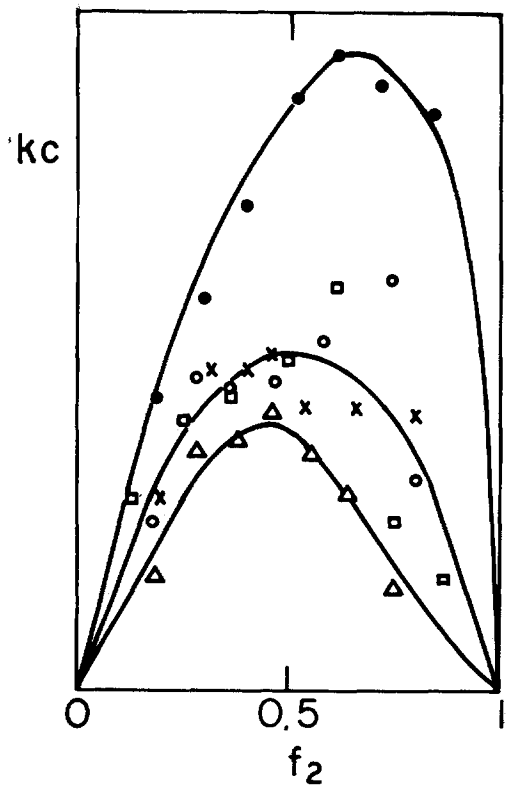


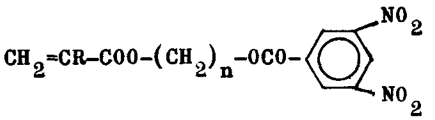
Figure 3. Intramolecular complex concentration for poly(HECM-co-DNBM) obtained in :

- ● toluene
- x methanol
- △ acetone
- □ dioxan
- o bulk

Figure 3 shows the effect of the copolymerization solvent. The copolymerization temperature was in all cases 60°C, except for bulk copolymerization (100°C).

Although the previous results also indicated that the synthesis in toluene gives the strongest intramolecular complex, this method clearly demonstrates that the toluene-obtained poly(HECM-co-DNBM) is twice stronger than the dioxane-obtained one and even stronger than the acetone-obtained one (see also table 1). The explanation is given by the low polarity of the solvent, which does not interact with any of the participant monomers, and also the poor solubility of the copolymer synthesized in the copolymerization solvent. This favours the alternating tendency, as demonstrated in the precedent paper (PERCEC et al. 1981c).

The influence of the distance between the complexing groups and the main chain is illustrated in figures 4 and 5. Here, the donor monomer was HECM and the acceptor monomers were :



	R = H	R = CH_3
n = 2	DNBA	DNBM
n = 3	DNBPA	DNBPM
n = 4	DNBBA	DNBBM

The intramolecular complex concentration is the highest for n = 3, lower for n = 4 and the lowest for n = 2 for the methacrylate-methacrylate pair (figure 4) following the decreasing side-chain flexibility order (PERCEC et al. 1981c), and for the methacrylate-acrylate pair (figure 5), complexes with n = 3 and n = 2 seem equally intense, whereas for n = 4 the complex concentration is slightly lower.

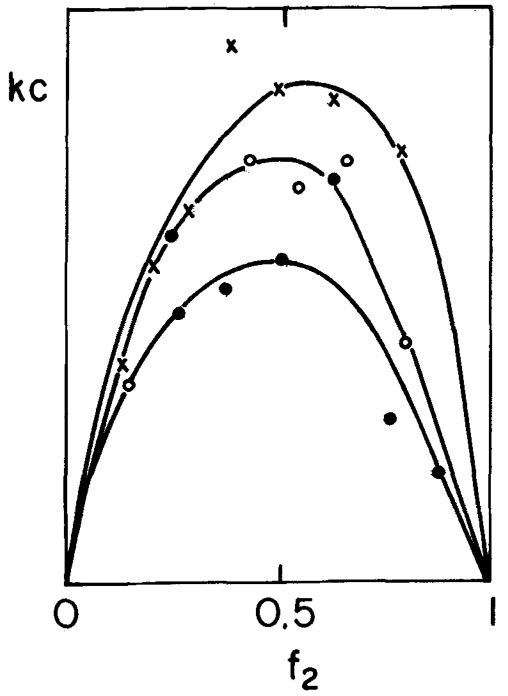


Figure 4. Intramolecular complex concentration for :

- ● poly(HECM-co-DNBM)
- x poly(HECM-co-DNBPM)
- o poly(HECM-co-DNBBM)

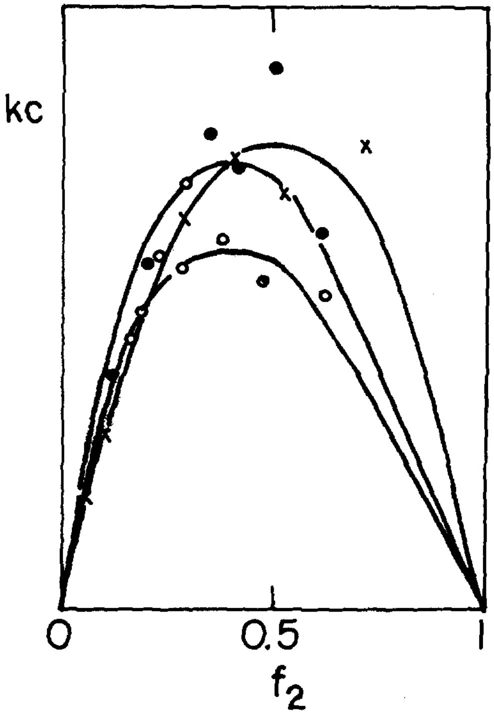


Figure 5. Intramolecular complex concentration for:

- ● poly(HECM-co-DNBA)
- x poly(HECM-co-DNBPA)
- o poly(HECM-co-DNBBA)

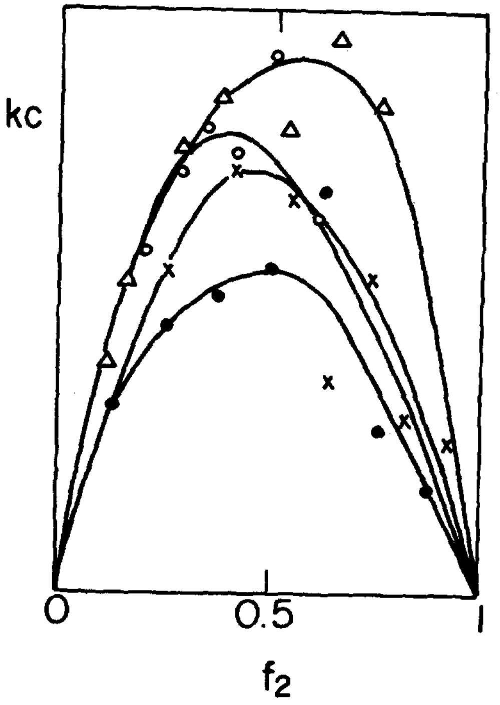


Figure 6. Intramolecular complex concentration for:

- ● poly(HECM-co-DNBM)
- x poly(HECA-co-DNBM)
- o poly(HECM-co-DNBA)
- △ poly(HECA-co-DNBA)

The most surprising results were obtained by the comparison of the intramolecular complexes from N-(2-hydroxyethyl)carbazolyl acrylate (HECA) and HECM as donors and DNBA and DNBM as acceptors (figure 6). Previous results showed that poly(HECA-co-DNBM) and poly(HECM-co-DNBM) present similar intramolecular complexation degrees (SIMIONESCU et al. 1980a,1981a), whereas the plot in figure 6 clearly indicates a dependence of the intramolecular complexation on the steric type of the monomer enchained.

Such a dependence was formerly found for other charge transfer complexes copolymers (PERCEC et al. 1980) and was supposed to disappear due to the increased distance between the complexing groups and the main chain, distance which permits complexation even in unlike stereostructures. This type of representation clearly shows that this assumption is not true.

Moreover, the order of increasing intramolecular complexation (methacrylate-methacrylate < acrylate-methacrylate < acrylate-acrylate) is the same as that found for the other systems. Because only by measuring the ^{1}H-NMR chemical shift one cannot make distinction between intra- and intermolecular complexation, these results have to be more accurately studied in order to explain the correlation found.

Other comparisons can be made on systems having HECM and HECA as donors and 2'-ethylacryl-(ETNFA) and 2'-ethylmethacryl-(ETNFM)-4,5,7-trinitro-9-fluorenon-2-carboxylate (SIMIONESCU et al. 1980b,1981b) - figure 7.

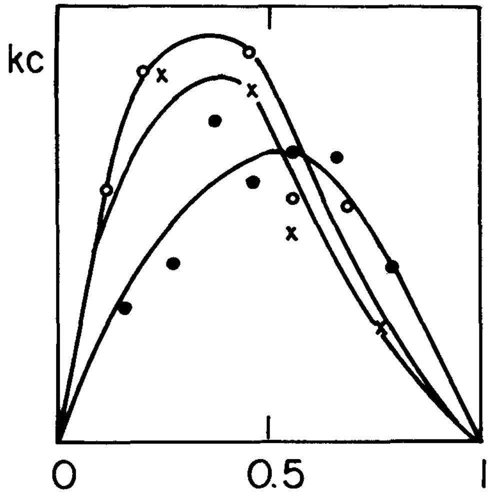


Figure 7. Intramolecular complex concentration for :

● poly(HECM-co-ETNFM)
x poly(HECM-co-ETNFA)
o poly(HECA-co-ETNFA)

Here, also, the weakest complex is given by the methacrylate-methacrylate pair. A smaller difference is obtained for N-ethyl-3-hydroxymethyl carbazolyl methacrylate (EHMCM) as donor when copolymerized with DNBA or DNBM (PERCEC et al. 1981b) - figure 8.

All systems having N-(2-hydroxyethyl)carbazole as donor and 3,5-dinitrobenzoate derivatives as acceptor are directly compared in table 1. The data in table 1 are reported using the weakest complex : poly(HECM-co-DNBM) obtained in acetone at 60°C as a reference (c(max) = 1). The strongest complex in this table was obtained from the same monomers at the same temperature, but copolymerization was performed in toluene (c(max) = 2.35). Other relatively strong complexes are poly(HECA-co-DNBA) obtained in dioxan at 60°C (c(max) = 2.03), poly(HECM-co-DNBPM) (c(max) = 1.85) and poly(HECM-co-DNBPA) (c(max) = 1.70).

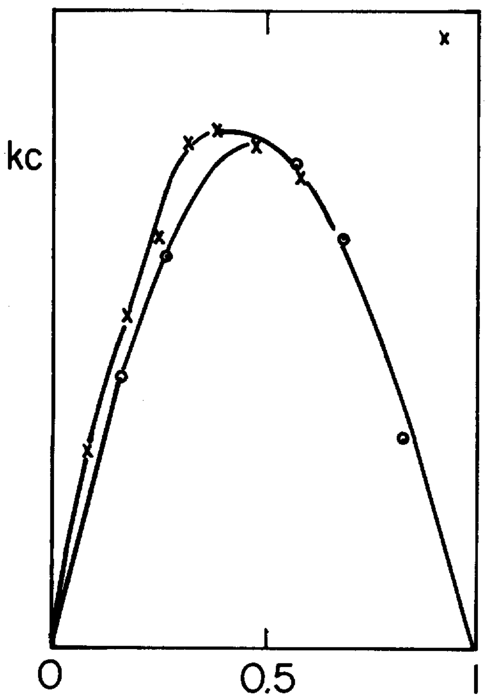


Figure 8. Intramolecular complex concentration for :

o poly(EHMCM-co-DNBM)
x poly(EHMCM-co-DNBA)

TABLE 1
Comparison of intramolecular complexation

Donor	Acceptor	Solvent	Temp.(°C)	c(max)	f_2(max)
HECM	DNBM	acetone	60	1	0.45
"	"	methanol	"	1.24	0.45
"	"	toluene	"	2.35	0.67
"	"	–	100	1.32	0.56
"	"	dioxan	"	1.08	0.50
"	"	"	80	1.27	0.52
"	"	"	60	1.21	0.47
"	DNBPM	"	"	1.85	0.57
"	DNBBM	"	"	1.57	0.52
"	DNBPA	"	"	1.70	0.53
"	DNBBA	"	"	1.32	0.37
"	DNBA	"	"	1.62	0.40
HECA	"	"	"	2.03	0.61
"	DNBM	"	"	1.52	0.49

It is to be noted that the f_2 value corresponding to c(max) is different for different systems. For a simple 1:1 complex, this value should have been $f_2 = 0.5$ in all cases. The explanation could be given by the most favourable sequence distribution, configuration and conformation corresponding to the f_2(max) value. But one has again to consider, besides the rather poor data precision, the concurrent intra- and intermolecular complexation.

More experimental data are needed to elucidate these findings.

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Received October 19, accepted November 11, 1982