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Copolymers with Pendant Electron-Donor and Electron-Acceptor Groups

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ABSTRACT

This paper is concerned with charge transfer complex properties of copolymers with pendant electron-donor and electron-acceptor groups obtained by radical copolymerization. The complexing groups were carbazolyl, anthryl, phenothiazinyl, and p-dimethylaminobenzyl as electron-donor groups, and picryl, dinitrophenyl, dinitrobenzoyl, and trinitrofluorenyl as electron-acceptor groups. The microstructure of such copolymers, including the tendency to alternating and coisotactic addition, together with the influence of monomer structure and reaction conditions, is discussed. Intramolecular complexation interactions are analyzed. These properties were measured by means of ^{1}H-NMR and electronic absorption spectra. Finally, some physical properties, e.g., color, solubility, density, and photoconductivity, are presented to illustrate the intramolecular and intermolecular complexation interactions. It is concluded that such copolymers are weak charge transfer complexes of the π-π type. They are of theoretical interest for study of the correlation between synthesis, structure, and properties, and of practical interest due to their optoelectric properties.

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INTRODUCTION

Copolymers with pendant electron-donor (D) and electron-acceptor (A) groups, or D-A copolymers as they will be called in this paper, are especially interesting due to their weak charge transfer complex (CTC) properties.

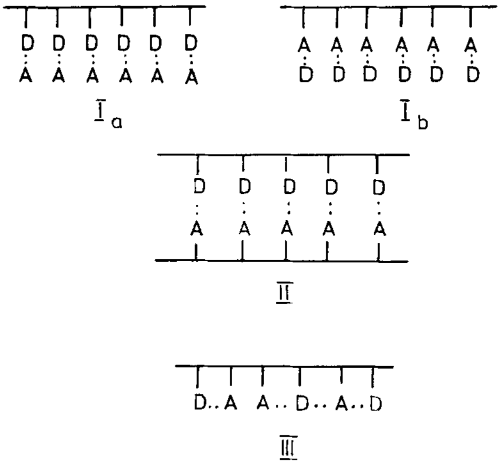
Theoretical and practical interest in CTC materials has been growing in the last few years due to their involvement in many chemical, physical, and biological phenomena. For example, the CTC role in polymerization and copolymerization has been previously observed [1, 2], and the polyvinylcarbazole-trinitrofluorenone (PVK-TNF) system, due to its high photoconductivity [3], is presently used in the electrophotographic industry. On the other hand, molecular doping of polyacetylene with a variety of donors and acceptors has led to a new class of materials known as "organic or synthetic metals" [4].

Recent research has also been directed toward the use of CTC for the conversion of solar energy to electrical energy [5].

MACROMOLECULAR CT COMPLEXES

Macromolecular complexes have at least one polymeric component; these can be considered as follows (Scheme 1):

Complexes between a donor (acceptor) polymer and a low molecular acceptor (donor) compound (Types I$_a$ and I$_b$).



SCHEME 1.

Complexes between a donor polymer and an acceptor polymer (Type II).

Complexes of a donor-acceptor copolymer type (Type III).

Type I_a complexes have been the most extensively studied, perhaps due to their ease of preparation and because the PVK-TNF complex is of practical interest. Nevertheless, the insertion of a low molecular compound into the matrix of a polymer (to obtain a CTC) diminishes the mechanical properties of the polymer, and the restoration of these properties by plasticization, for example, seriously deteriorates photoconductivity. Although very few studies have been published, macromolecular CTC of Types II and III might overcome these disadvantages.

The present paper is concerned only with D-A copolymers. These copolymers behave in dilute solutions as intramolecular CT complexes (Fig. 1).

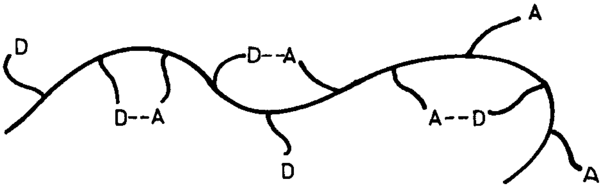


FIG. 1. Intramolecular complexation interactions for a D-A copolymer in solution.

SYNTHESIS OF D-A COPOLYMERS

D-A copolymers have been obtained by three methods.

Polymer Analogous Reaction Method. The partial nitration of polyacenaphthalene [6], polyvinylnaphthalene [7], and polyvinylcarbazole [8] leads to D-A copolymers. Their CTC properties are proved by their color and increased photoconductivity. Gipstein et al. [9] obtained vinylfluorene-vinylfluorenone copolymers by a partial oxidation of polyvinylfluorene. They also synthesized a terpolymer of the vinylfluorene-vinylfluorenone-vinylcarbazole type by oxidation of a vinylfluorene-vinylcarbazole copolymer. Chang et al. [10] obtained D-A copolymers by starting from vinylcarbazole-vinyl acetate or vinylcarbazole-acryloyl chloride copolymers, and Schulz [11] synthesized polyvinyl alcohol acetal with naphthyl and carbazolyl donor groups and dinitrobenzoyl and trinitrofluorenyl acceptor groups. All these copolymers showed a photoconductivity higher than that of PVK.

Polycondensation between a Donor Monomer and an Acceptor Monomer. Tsuchida et al. [12] used the Mannich reaction, starting from dinitrotoluene, 1,3-bis-4-piperidylpropane, and formic aldehyde to yield a D-A copolymer, and Schulz [13] obtained CTC polyesters from spirocyclopropanes of tetranitrofluorenone and fluorene.

Radical Copolymerization of Donor-Acceptor Monomer Pairs. Kadoma et al. [14] showed the possibility of copolymerizing picryl methacrylate with donor monomers although picryl methacrylate does not homopolymerize. The first D-A copolymer obtained by radical copolymerization was reported by Yang and Gaoni [15] who used 2- and 4-vinylpyridine as donor monomers and trinitrostyrene as the acceptor monomer. However, their results were contested by Butler [16]. Recently, Stolka and Turner [17] obtained a D-A copolymer by the copolymerization of anthracene and trinitrofluorenone methacrylates.

Radical copolymerization could be the most convenient method to obtain D-A copolymers, considering that it allows (theoretically at least) a method to improve the degree of intramolecular complexation by an improvement of copolymer microstructure.

The present paper is mainly concerned with the CTC properties for a series of D-A copolymers containing such electron-donor groups as carbazolyl, anthryl, phenothiazinyl, and p-dimethylaminobenzyl, and such electron-acceptor groups as picryl, dinitrophenyl, dinitrobenzoyl, and trinitrofluorenyl. The structures of the synthesized monomers and of the copolymer systems studied are shown in Fig. 2.

As a rule, the copolymerizations were carried out in dioxane solution at 60°C by using 1% AIBN as the initiator and a total monomer concentration of 0.5 mol/L. To evidence the influence of reaction conditions on D-A copolymer properties, solvent, temperature, and monomer concentration were varied for several systems. All syntheses were performed under argon in sealed ampules. The copolymers were precipitated with methanol, dried, and reprecipitated with methanol from tetrahydrofuran and dioxane solutions. The copolymer composition and the degree of complexation were estimated by means of ^{1}H-NMR spectra recorded at 60 MHz. Other experimental details can be found in the references given for each copolymer.

MICROSTRUCTURE OF D-A COPOLYMERS

Since the Kelen-Tüdös plots of the copolymerization systems studied are curves rather than straight lines, the copolymerizations do not represent the terminal model. Such behavior can be explained by the formation and participation in the reaction of intermonomeric CT complexes. As a consequence, a large tendency to alternation and coisotacticity is expected when the intermonomeric CT complexes are strong and highly reactive. On the other hand, this tendency should not be pronounced considering that the side chains are too long and flexible to have a stable tightness between the two vinyl groups of an intermonomeric CT complex.

Alternating Tendency and the Influence of Various Factors

The alternating tendency can be indirectly deduced from the copolymerization diagrams (Fig. 3). As is well known, an alternating copolymer shows a copolymerization diagram similar to those given in Fig. 3(A), the alternation being as high as the middle part of the diagrams is flat and extensive.

Influence of Substitution at the Vinyl Group. This is illustrated in Fig. 3(A), where the following order of alternating tendency is observed: methacrylate-methacrylate $<$ methacrylate-acrylate $<$ acrylate-acrylate.

Influence of Side-Chain Length. For the systems considered, the number of bonds separating the donor and acceptor groups from the main chain is as follows: 5 and 3 for HECM-DNPM, 5 and 7 for HECM-DNBM, and 5 and 9 for HECM-DNBBM (Fig. 3B). The result is that the alternating tendency increases with an increase of the length of the side chains. This conclusion seems to be true, at least for the methacrylate-methacrylate systems.

It should be mentioned that the HECM-DNBM copolymer obtained under the conditions given in Fig. 3(B) shows an azeotropic composition, therefore the reactivity ratios r_1 and r_2 have values equal to unity.

Influence of Copolymerization Conditions. By considering Figs. 3(C), 3(D), and 3(E), the following observations can be made:

The alternation tendency increases with the dielectric constant of the reaction medium (Fig. 3C).

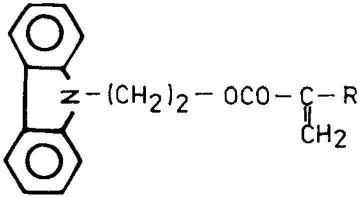
An increase of the reaction temperature (Fig. 3D) and a decrease of monomer concentration (Fig. 3E) causes a decrease of alternation.

Influence of Complexing Groups. Although expected, such an influence is not too evident. According to Fig. 3(F), the composition diagrams correspond to the following reactivities:

$r_1 < 1$ and $r_2 > 1$ for the systems PtA-DNBM and HECA-DNBM.
$r_1 = r_2 = 1$ for the HECM-DNBM system.
$r_1 = r_2 < 1$ for the AMMA-DNBA system.
$r_1 \neq 0$ and $r_2 = 0$ for the HECM-PM system.

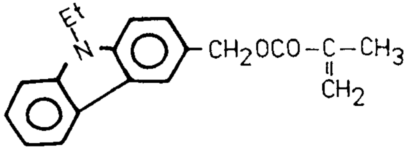
The result is that the AMMA-DNBA copolymer is the most alternating system of the systems studied.

Donor monomers

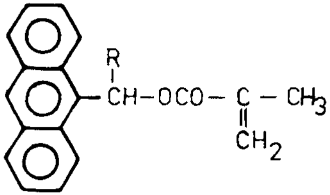


H HECA

CH_3 HECM

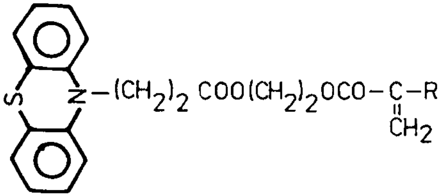


EHMCM



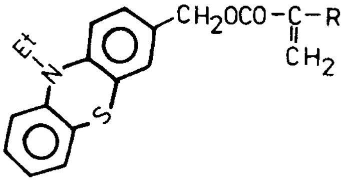
H AMMA

CH_3 AEMA



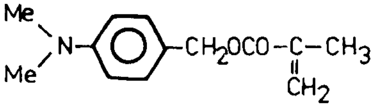
H PtA

CH_3 PtM



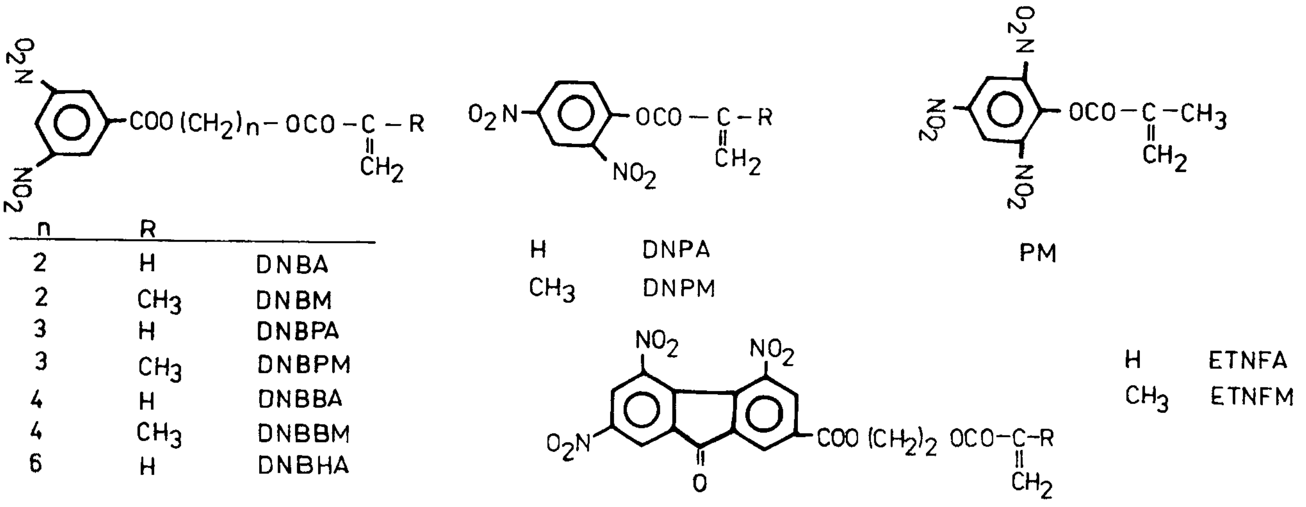
H PtEA

CH_3 PtEM



DMABM

Acceptor monomers



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

H	DNPA
CH_3	DNPM

PM

H	ETNFA
CH_3	ETNFM

Copolymer systems and references

HECA — DNBA (18)
HECA — DNBM (19)
HECA — DNPA (20)
HECA — DNPM (21)
HECA — ETNFA (22)
HECM — DNBA (18)
HECM — DNBM (19)

HECM — DNPA (20)
HECM — DNPM (23)
HECM — DNBPA (M) (24)
HECM — DNBBA(M) (24)
HECM — PM (25)
HECM — ETNFA (M) (26)
EHMCM— DNBM (27)

AMMA — DNBA (28)
AMMA — DNBM (29)
AMMA — DNBHA (28)
AEMA — DNBM (29)
PtA (M)— DNBM (30)
PtEA (M)— DNBM (31)
DMABM — DNBA(M) (32)

FIG. 2. Monomer structures, systems of D-A copolymers, and references.

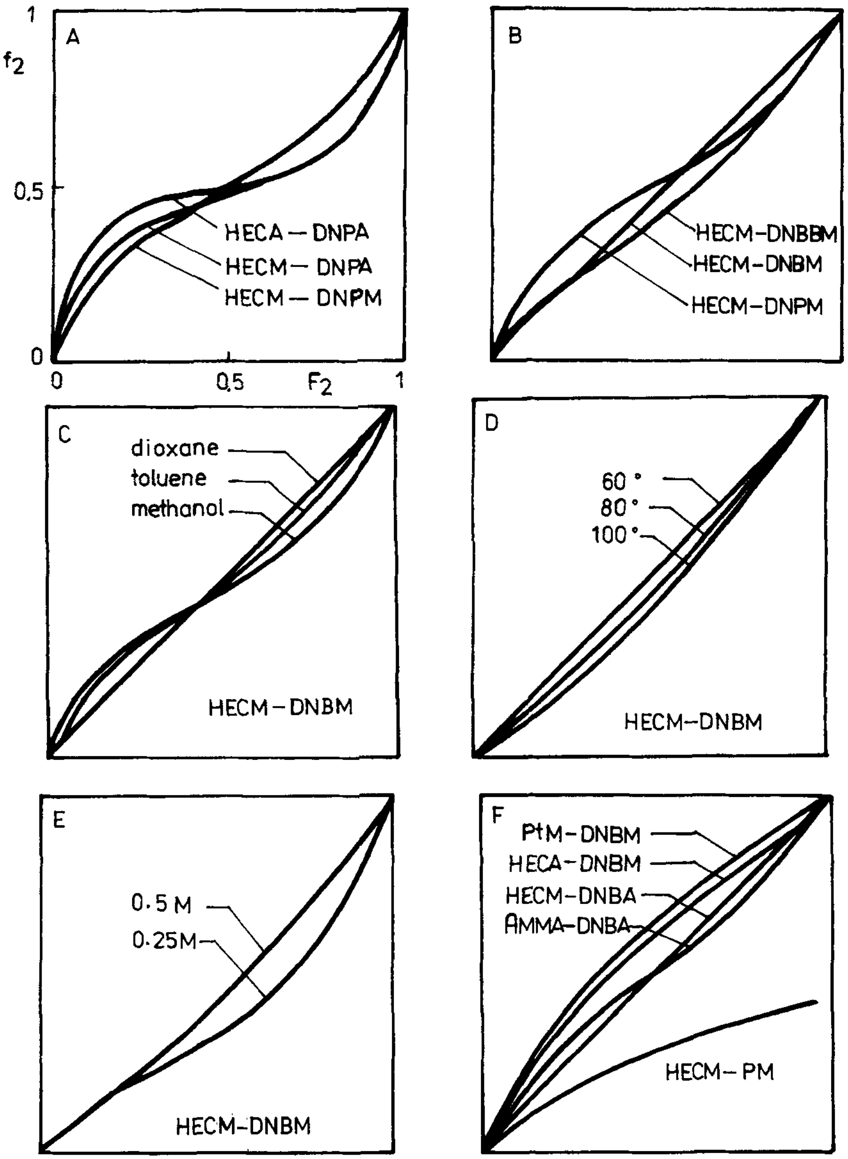


FIG. 3. Composition diagrams for several synthesized D-A copolymers. Reaction conditions are: A and B, dioxane, 60°C, 0.5 M; C, 60°C, 0.5 M; D, dioxane, 0.5 M; E, dioxane, 100°C; and F, dioxane, 60°C, 0.5 M. F_2 and f_2 are the molar fractions of acceptor structural units for the initial feed and the copolymer, respectively. Copolymer composition were determined from ^{1}H-NMR spectra. The figures illustrate the influence of different parameters on the alternating tendency as follows. A: The substitution at the vinyl group. B: The length of the side chains. C, D, and E: The reaction conditions (solvent, temperature, and monomer concentration, respectively). F: Complexing groups.

The Coisotacticity Tendency

The only method that allows some conclusions on the configuration of D-A copolymers to be drawn is ^{1}H-NMR spectroscopy through analysis in terms of sequence distribution and configuration of the α-methyl signal. Such an analysis was made of the HECM-DNBM and HECA-DNBM systems [33]. By using a signal assignment similar to that made in the case of methyl methacrylate-methacrylic acid copolymers and the values of homopolymer configurational parameters, namely $\sigma_{11} = 0.21$ for polyHECM and $\sigma_{22} = 0.26$ for polyDNBM, the following values expressing the coisotactic alternating addition probability were found: $\sigma = 0.2$ for the HECM-DNBM system and $\sigma = 0.7$ for the HECA-DNBM system.

These values indicate that methacrylate-methacrylate systems are characterized by a pronounced tendency to cosyndiotacticity because $\sigma < 0.5$, while the acrylate-methacrylate systems are more coisotactic with $\sigma > 0.5$. It is assumed that the coisotactic tendency is more pronounced in acrylate-acrylate systems, but this fact cannot be demonstrated by ^{1}H-NMR spectroscopy.

On the other hand, because $\sigma \neq (\sigma_{11} \cdot \sigma_{22})^{1/2}$, it has to be assumed that not only the monomer's steric effects determine the addition, but there are also other parameters, especially for D-A copolymers where the role of intermonomeric CTC is quite important. Unfortunately, configurational analysis cannot be correlated with various structural and synthetic parameters because the majority of D-A copolymers show ^{1}H-NMR spectra of low resolution.

The microstructure of D-A copolymers with pendant electron-donor and electron-acceptor groups is influenced by monomer structure and copolymerization conditions, but a clear correlation of the two factors has not been established. A rough measure of the alternation and coisotacticity of such copolymers might be the degree of intramolecular complexation. However, as shown further on, even such a correlation is not rigorous because: 1) estimates of the degree of complexation have a low precision, and 2) the length and flexibility of side chains may cancel the dependence of the degree of complexation on the cotacticity. In fact, one of the main ideas of our studies was to increase the flexibility of side chains to obtain macromolecular CTC with donor-acceptor interactions independent on the configuration of the main chain.

INTRAMOLECULAR INTERACTIONS BETWEEN ELECTRON-DONOR GROUPS AND ELECTRON-ACCEPTOR GROUPS

Considering that both electron-donor and electron-acceptor groups are of the π type, complexation interactions must lead to parallel arrangements of them. These interactions are evidently of both the intramolecular and intermolecular types, with the former expected to predominate in dilute solutions. Therefore, they might be evidenced by electronic absorption spectra and NMR spectra. In a recent paper [34] it was shown that pure intramolecular interactions should be present in solutions with a concentration lower than about 16 mg/mL (1.6%), this value being the upper limit for a linear dependence between CTC band absorbance and solution concentration. However, as shown further on, intramolecular interactions may also be studied by means of ^{1}H-NMR spectra, although in this case the solution concentration is about 3-5%. In fact, the main difference between intramolecular and intermolecular interactions is that the former are dependent on copolymer microstructure, at least in the case of short and/or rigid side chains.

The Study of Complexation Interactions by Means of Electronic Absorption Spectra. Although all copolymers presented in Fig. 2 are colored, the CTC band is not usually observed due to its large broadening and/or to overlapping from the most intense band characteristic of uncomplexed chromophores (Fig. 4A). Such a band is placed at $\lambda \leq 500$ nm, and is therefore in the range of π-π transitions. As expected, the absorbance of CTC band show a maximum at 1:1 composition for all the copolymers studied (Fig. 4B). Also, the absorbance of a CTC band decreases linearly as the temperature increases (Fig. 4B). This means that the intensification of molecular motion leads to the detachment of CTC, and therefore the complexation process is in equilibrium with the thermal motion of the solvent and copolymer molecules.

One cannot estimate, even approximately, the degree of complexation from the CTC band because it is too poorly resolved.

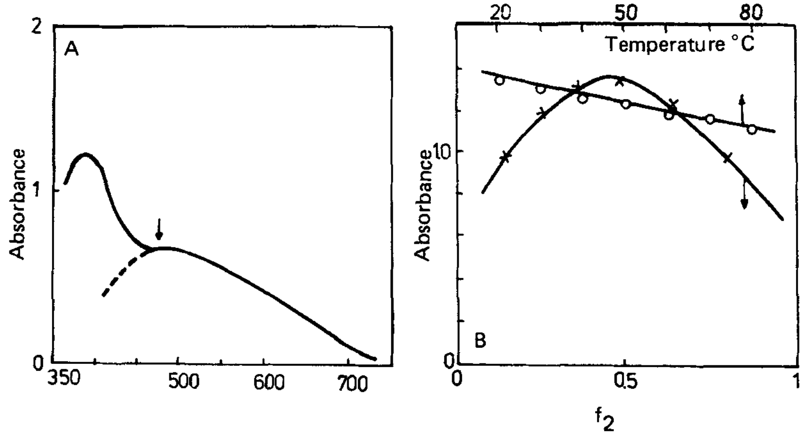


FIG. 4. The D-A interaction description by means of the electronic absorption spectra for PtEM-DNBM copolymers: the CTC band (A) and the dependence of the CTC band absorbance on copolymer composition and temperature (B).

Study of Complexation Interactions by Means of ^{1}H-NMR Spectroscopy. Because complexation leads to a parallel arrangement between the plane surfaces of donor and acceptor groups, the degree of complexation, namely the strength and the concentration of complexes, can be correlated with the chemical shifts of the aromatic protons. In the case of low molecular aromatic CTC, it was found that the chemical shifts of aromatic protons decrease linearly with the degree of complexation, and their range of variation is relatively small (about 1 ppm). This fact suggests that such chemical shifts are mainly determined by the ring-current effects (and therefore by the parallel arrangement of complexing groups), and not by the charge transfer [35]. This conclusion is based on the fact that the proton chemical shifts in both donor and acceptor groups are not only numerically similar, but are also of the same sign, i.e., upfield from the positions characteristic of the uncomplexed states. If charge transfer significantly contributes to chemical shift variation, a downfield shift of proton signals in the donor group on complex formation should be expected.

The ^{1}H-NMR method for the characterization of complexation is presented in Fig. 5. The signals of the aromatic protons in acceptor

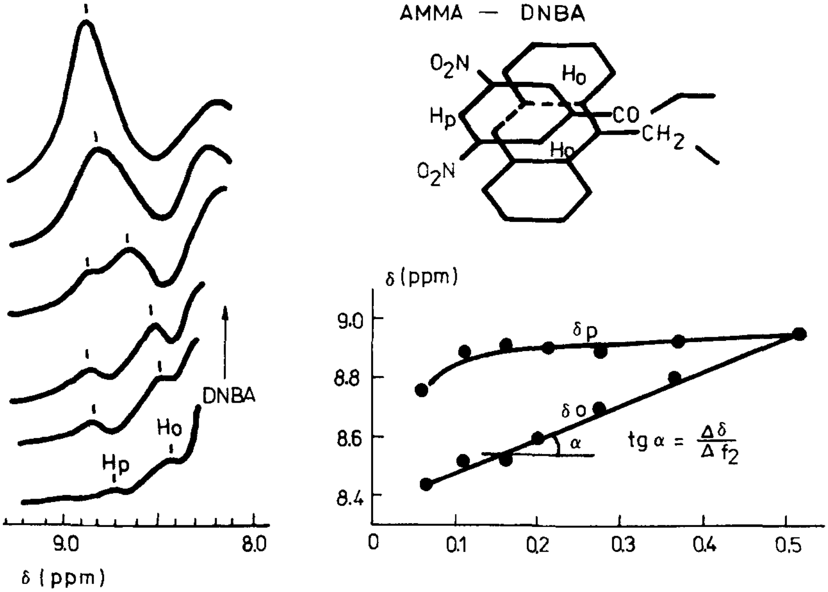


FIG. 5. The dependence of chemical shift of aromatic protons of acceptor groups in the AMMA-DNBA copolymers on composition. The NMR spectra were obtained in the following conditions: 60 MHz, dioxane, 90°C.

TABLE 1. Relative Values of the Degree of Complexation Measured by Means of the ^{1}H-NMR Spectra for Different D-A Copolymers[a]

Copolymer	Synthesis conditions	Recording conditions of spectra	$\Delta\delta/\Delta f_2$, ppm	Length of side chains[b]	
				n_d	n_a
HECM-DNBM	Dioxane, 60°C, 0.5 M	DMSO-d_6, 150°C	0.33	5	7
HECM-DNBPM	Dioxane, 60°C, 0.5 M	DMSO-d_6, 150°C	0.41	5	8
HECM-DNBBM	Dioxane, 60°C, 0.5 M	DMSO-d_6, 150°C	0.45	5	9
HECA-DNBM	Dioxane, 60°C, 0.5 M	DMSO-d_6, 150°C	0.33	5	7
HECA-DNBPM	Dioxane, 60°C, 0.5 M	DMSO-d_6, 150°C	0.45	5	8
HECA-DNBBM	Dioxane, 60°C, 0.5 M	DMSO-d_6, 150°C	0.50	5	9
HECM-DNBM	Toluene, 60°C	DMSO-d_6, 150°C	0.47	5	7
HECM-DNBM	Dioxane, 60°C	DMSO-d_6, 150°C	0.36	5	7
HECM-DNBM	Bulk, 100°C	DMSO-d_6, 150°C	0.40	5	7
HECM-DNBM	Dioxane, 100°C	DMSO-d_6, 150°C	0.23	5	7
HECM-PM	Dioxane, 60°C	$CDCl_3$, 20°C	2.3	5	3
HECM-PM	Dioxane, 60°C	$CDCl_3$, 60°C	1.8	5	3
AMMA-DNBA	Dioxane, 60°C	Dioxane, 90°C	1.02	4	7
AMMA-DNBHA	Dioxane, 60°C	Dioxane, 90°C	0.76	4	10
AMMA-DNBM	Dioxane, 60°C	Dioxane, 90°C	0.86	4	7
AEMA-DNBM	Dioxane, 60°C	Dioxane, 90°C	0.23	4	7

[a] Values of the $\Delta\delta/\Delta f_2$ slope where δ is the chemical shift of the aromatic proton in the acceptor groups and f_2 is the molar fraction of the acceptor groups.

[b] n_d and n_a are the number of bonds which separate the donor and acceptor groups, respectively, from the main chain.

groups are considered because they are relatively simple and are located at the largest chemical shifts. The $\Delta\delta/\Delta f_2$ slope of the dependence of chemical shift against copolymer composition was chosen as the measure of the degree of complexation. One other measure of this parameter could be the product between chemical shift variation (relative to the homopolymer) and copolymer composition [36].

The influence of several factors on complexation is presented further on. It is supposed that the degree of complexation as determined by ^{1}H-NMR spectra is related to intramolecular interactions, although the solution concentration used (3-5%) might be too high for intermolecular interactions to be neglected.

Influence of Copolymer Structure. According to the data given in Table 1, the degree of complexation is a little higher for methacrylate-acrylate than for methacrylate-methacrylate copolymers. Also, an increase is observed when the side chain lengths increase up to 6-7 bonds, but if the side chains are too long (see the AMMA-DNBHA system [28]) the dependence is reversed. It appears that complexation is optimum when the donor and acceptor groups are equally spaced from the main chain. However, such a conclusion has not been proved.

Influence of Complexing Groups. It appears that the degree of complexation increases in the following order: carbazolyl-dinitrobenzoyl < anthryl-dinitrobenzoyl < carbazolyl-picryl.

In addition, by comparing the AMMA-DNBM and AEMA-DNBM systems, it is seen that the presence of substituents near the complexing groups causes a decrease of complexation, perhaps by increasing the distance between the donor and acceptor groups of a CTC.

Influence of Copolymerization Parameters. By considering the HECM-DNBM system as obtained in different solvents and at various temperatures, it appears that complexation decreases with the solvent dielectric constant and an increase of temperature.

Influence of Temperature. By comparing the values of $\Delta\delta/\Delta f_2$ slope obtained at 20 and 60°C for the HECM-PM system, it is seen that complexation decreases with temperature. This observation confirms the fact that the complexation process is in equilibrium with thermal molecular motion.

Correlation between the Degree of Complexation and Copolymer Microstructure. Although both the degree of complexation, measured as the $\Delta\delta/\Delta f_2$ slope in NMR spectra, and the microstructural parameter are rather imprecisely determined, the following correlations are observed: 1) the degree of complexation and the coisotacticity tendency are similarly influenced by the steric hindrance of the main chain, by the length of the side chains, and by the synthesis conditions (temperature and solvent); however, 2) it is not yet possible to reach a clear conclusion concerning the influence of the complexing groups.

PHYSICAL PROPERTIES INDUCED BY THE COMPLEXATION

Several properties of D-A copolymers as determined from both intra molecular and intermolecular interactions are presented.

Absorption in Visible Range and Color

Although the parent homopolymers are colorless, all the D-A copolymers presented in this paper are colored as follows: systems of carbazolyl or anthryl with dinitrobenzoyl are orange, systems of carbazolyl with picryl are pink, and systems of phenothiazinyl with dinitrobenzoyl are pale violet. As previously stated, except for the phenothiazinyl-dinitrobenzoyl systems which show a resolved CTC band with a maximum at 490 nm (Fig. 4A), the absorption band in the visible range is very broad for all synthesized copolymers.

Other observations are as follows: the color intensity decreases with temperature, increases with sample compactness, and shows a maximum for 1:1 compositions (Fig. 4B).

Solubility

D-A copolymers are soluble only in polar solvents (tetrahydrofuran, dimethylsulfoxide, dimethylformamide, dioxane) and upon heating, unlike the parent homopolymers which are soluble in common solvents (aromatic and/or halogenated hydrocarbons). The solubility is minimal in the case of copolymers of 1:1 composition and is much lowered if the copolymers are compressed or obtained from solution by a very slow evaporation of solvent [37].

The following interesting behavior was also observed. The copolymers precipitate at slight heating (40-60°C) of a solution which is clear at room temperature, and redissolution can be obtained only at temperatures higher than 100-110°C. Such behavior, which is more evident for copolymers of 1:1 composition, can be explained as follows: Clear solutions at room temperature are characterized only by intramolecular D-A interactions. Slight heating increases the probability to collisions between different chains to occur, and therefore precipitation is caused by intermolecular D-A interactions. Redissolution at high temperatures is due to decomplexing of the intermolecular complexes.

Density

A plot of density against composition is given for a D-A copolymer in Fig. 6. The plot is not a straight line but shows an important maximum for a 1:1 composition. This may be explained by the density of the complexation state which is a maximum for such a composition.

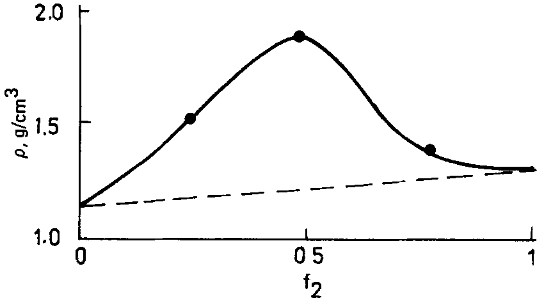


FIG. 6. The dependence of sample density on copolymer composition for the HECM-DNBM system.

Viscoelastic Properties

Both the modulus and the dynamic viscosity show maximum values for a 1:1 composition [38]. Such maxima are more evident at low temperatures and low frequencies.

Processing in Thin Films

The films cast from solutions under ordinary conditions show cracks. However, it is possible to obtain good films if solvent evaporation and cooling are performed very slowly. Film adherence at metal- or glass-type supports is rather low.

Electrical Conductivity and Photoconductivity

Conductivity in the dark is very low (10^{-16} to $10^{-17}\,\Omega^{-1}\cdot\text{cm}^{-1}$), but D-A copolymers are distinguished from common insulating polymers by their obvious photoconductivity properties.

Photoconductivity of Thick Samples (Pellets). The first photoconductivity measurements were made on pellet samples because of the difficulties met in obtaining films [39]. The qualitative dependence of photoconductivity on copolymer composition is given in Fig. 7(A). Such a dependence, with its two relatively small maxima, can be explained by considering that 1) the carrier mobility (μ) shows a minimum at 1:1 composition because the blockages of conduction channels are at a maximum in these conditions, and 2) the photogeneration has a maximum at 1:1 composition, with the density of excited CTC states reaching maximum values (Fig. 7B).

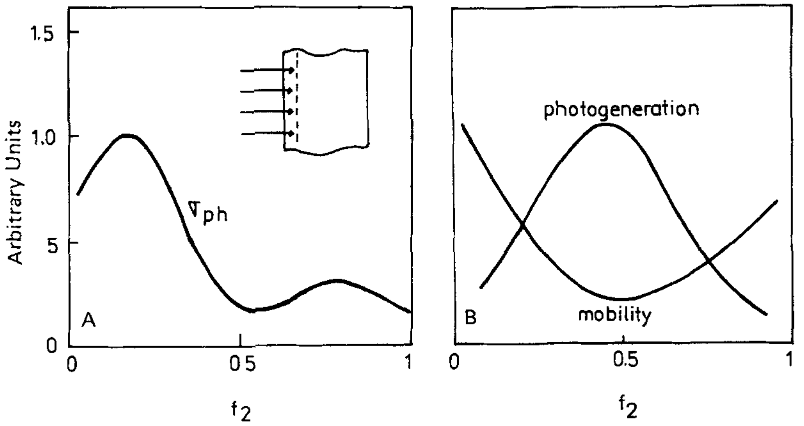


FIG. 7. Photoconductivity against copolymer composition for thick samples (pellets) of a D-A copolymer. A: The qualitative dependence. B: The dependence assumed for photogeneration and mobility. The photoconductivity scale is given in arbitrary linear units.

Photoconductivity of Thin Films [40]. The dependence on copolymer composition (Fig. 8A) shows a strong maximum at 1:1 composition. The maximum corresponds to the maximum of carrier photogeneration. On the other hand, it can be assumed that the dependence of drift mobility on copolymer composition is different in the case of thin films where the excitation of CTC states is realized in the entire sample volume, whereas in thick samples the excitation takes place only in a thin, superficial layer.

Dependence of the Photoconductivity on the Wavelength of Irradiation. It was observed that the maximum photoconductivity of copolymers is at wavelengths longer (50-100 nm) than those corresponding to the parent homopolymers [40].

The photoconductive properties may be used for a quantitative estimation of the degree of D-A complexation in the solid state. However, it is necessary to overcome the difficulty of preparing films of proper quality for all the copolymers studied.

SOME CONCLUSIONS

Copolymers of the poly(donor-co-acceptor) type with pendant electron-donor and electron-acceptor groups spaced by more than 3 bonds from the main chain are weak CTC because, for example, the NMR chemical shifts are mainly determined by ring-current effects and not by charge transfer.

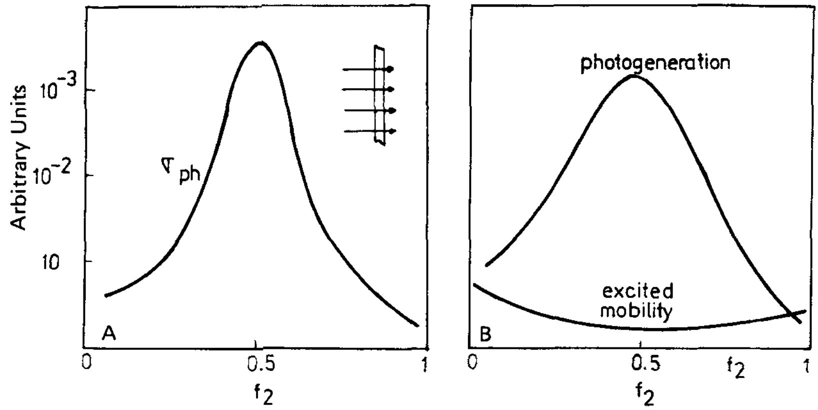


FIG. 8. Photoconductivity vs copolymer composition for thin samples (films) of a D-A copolymer. A: The qualitative dependence. B: The dependence assumed for photogeneration and mobility. The photoconductivity scale is given in arbitrary logarithmic units.

Their intramolecular CTC character can be shown by means of the electronic absorption and ^{1}H-NMR spectra. In addition, these methods allow a rough correlation between the degree of intramolecular complexation and the microstructure of the copolymers.

Several physical properties, e.g., color, solubility, density, and photoconductivity, show (as expected) that the density of intra- and intermolecular CTC is a maximum for copolymers of 1:1 composition.

The donor-acceptor copolymers are primarily of theoretical interest, but they may have many interesting applications due to, for example, their optoelectric properties and the possibility of controlling their microstructure, and therefore their mechanical properties.

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