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STUDIES OF THE MECHANISM OF COPOLYMERIZATION OF ELECTRON-DONOR DIENES AND ACRYLONITRILE

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ABSTRACT

In the copolymerizations of acrylonitrile with 1-ethoxy-1,3-butadiene and 1-diethylamino-1,3-butadiene, the resulting copolymers were found to have a highly alternating structure. Their monomer reactivity ratios were determined by the Fineman-Ross and Kelen-Tüdős methods. A mechanism for this alternating copolymerization system is suggested on the basis of chemical shift differences between the head-to-tail and head-to-head monomer sequence distributions.

INTRODUCTION

General Background

When electron donors and electron acceptors are brought together, they usually form electron donor-acceptor complexes to various extents. The term "electron donor-acceptor complex" is used to describe a wide variety of intermolecular complexes. Its range comprises Lewis acid-Lewis base interactions, ion pairs, and charge-transfer complexes. The enthalpies of dissociation of

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these complexes are much smaller than those of ordinary chemical reactions and are similar to those of hydrogen bonds and van der Waals forces.

In 1949, Benesi and Hildebrane [1] measured the ultraviolet spectra of iodine and benzene in *n*-heptane solutions and discovered a new absorption band uncharacteristic of either of the component molecules. Later Mulliken [2, 3] successfully developed a now widely accepted theoretical description of these phenomena. Mulliken's contribution has stimulated a wide variety of theoretical and experimental work in this area.

Mulliken's Valence Bond Treatment

On the basis of the valence bond theory, Mulliken described a complex that exists in a resonance form between the no-bond and the dative states of the donor molecule (D) and the acceptor molecule (A):

$$D + A \overset{K}{\rightleftharpoons} [\underset{\text{no bond}}{(D, A)} \longleftrightarrow \underset{\text{dative}}{(D^+, A^-)}] \tag{1}$$

where K is the formation constant of the complex.

The wave function of the complex can be expressed as a linear combination of wave functions of the no-bond state and the dative state. For the ground state

$$\begin{gathered}\psi_N = a\psi_0(D, A) + b\psi_1(D^+, A^-)\\ \text{with } a \gg b\end{gathered} \tag{2}$$

and for the excited state

$$\begin{gathered}\psi_E = b^*\psi_1(D^+, A^-) - a^*\psi_0(D, A)\\ \text{with } b^* \gg a^*\end{gathered}$$

where $\psi_0(D,A)$ is the wave function for the molecular complex which is held together by several physical electrostatic forces involving dipole-dipole, dipole-induced dipole, London dispersion, and hydrogen bonding types. The term $\psi_1(D^+,A^-)$ correlates with a wave function for the complex where one electron has been entirely transferred from the donor molecule to the acceptor molecule. The transition between these two states yields the characteristic charge-transfer absorption band. The term "charge-transfer complex" is usually given to this association pair.

Molecular Orbital Treatment

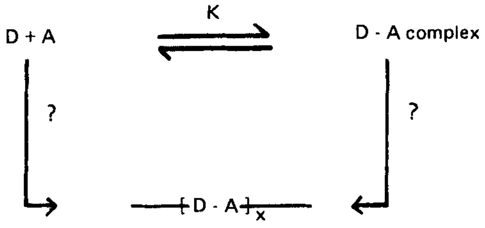
About the same year, an alternative approach to this intermolecular charge-transfer transition was proposed by Dewar [4] and Fukui [5], respectively.

In their approaches, the complex is treated as a π-complex which is formed by the interaction of the π-orbitals of the donor and the acceptor. Since the interaction between donor and acceptor is very small, the charge-transfer interaction can also be treated by the perturbation method.

Interactions between occupied bonding orbitals of donors and acceptors produce to change in their total energy and no net transfer of charge between donor and acceptor. Interactions of the occupied orbitals of the donor with the unoccupied antibonding orbitals of the acceptor lower the former and elevate the latter, leading to a net stabilization with a transfer of negative charge from donor to acceptor. Interactions of the occupied orbitals of the acceptor with the unoccupied antibonding orbitals of the donor similarly produce stabilization with a net charge transfer in the opposite direction. These interactions are inversely proportional to the energy gap between the interacting orbitals. The donor is usually recognized as having the highest-energy occupied molecular orbital (HOMO) and the acceptor is recognized as having the lowest-energy unoccupied molecular orbital (LUMO). The interaction between LUMO and HOMO has been thought to play an important role in many organic reactions.

Alternating Copolymerization

Alternating copolymerizations are characterized by the fact that a nearly 1:1 molar ratio of the comonomers is found in copolymers produced from a wide variety of comonomer mole fractions in the feed. The possible reaction pathways are as follows [6]:



Alternating copolymer

On the basis of these possible reaction pathways, three mechanisms have been proposed to explain this strong alternation tendency between the electron donor and the electron acceptor.

In 1946 Bartlett and Nozaki [7] proposed the first mechanism, in which copolymerization occurs via a stable monomer complex composed of the two monomer units. This mechanism has been supported by the work of Butler and coworkers [8-11] (maleic anhydride-divinyl ether and maleic anhydride-furan copolymers), Caze and Loucheux [12] (maleic anhydride-vinyl acetate copolymer), Goethals and coworkers [13] (maleic anhydride-benzofuran, maleic anhydride-indole, maleic anhydride-benzothiophene copolymers), Yamashita and coworkers [14, 15] (maleic anhydride-*p*-dioxene, maleic anhydride-1,2-dimethoxyethylene copolymers), and Gaylord and coworkers [16, 17] (maleic anhydride-conjugated diene copolymers). This mechanism is also called the "complex" mechanism.

Walling [18] proposed the second mechanism, in which electrostatic interactions between differently polarized monomers and radicals decrease the activation energy for alternating chain propagation. This is also called the "free monomer" mechanism.

The third mechanism was proposed by Shirota [19] and Tsuchida [20], respectively. This involves the participation of both free monomers and the charge-transfer complex monomer in the propagation steps. This mechanism originates from the fact that the initial copolymerization rate does not necessarily become maximum at a monomer feed ratio 1:1 where the concentration of the charge-transfer complex attains its maximum, which is inconsistent with the second mechanism.

Copolymerization of Conjugated Dienes and Dienophiles

In 1970, Butler and coworkers [9] studied the copolymerization of furan and maleic anhydride, and found that a 1:1 copolymer of these comonomers was produced, regardless of the monomer feed ratio. The presence of a donor-acceptor complex between the monomers was observed by NMR and UV methods. Therefore, they proposed that the polymerizations proceed by homopolymerization of this complex to produce an alternating sequence in the copolymer.

In 1976 [10] and 1981 [11], Butler and Ragab reported further studies on the mechanism of this copolymerization, and showed that the copolymer was comprised of alternating monomer units. They also studied the copolymerization of a number of furan derivatives with maleic anhydride, comparing the copolymer microstructures with those of model compounds. They made a comparative study of various donors and acceptors related to furan and maleic anhydride, and concluded that the trend among the initial polymerization rates was analogous to that among the equilibrium constants for complex formation. On the basis of their studies, they suggested that the donor-acceptor complex is the active polymerizing species.

Gaylord and coworkers have made wide-ranging studies of the free radical copolymerization of maleic anhydride with conjugated dienes, butadiene [16], pentadienes [17], and cyclopentadienes [21]. They postulated that the cyclic adduct and the alternating copolymer arise from a common intermediate, i.e., the charge-transfer complex, as a result of intramolecular and intermolecular reactions. The cyclic adduct was proposed to be formed from the complex in the ground state, and the alternating copolymer from the complex in the excited state.

In order to gain further insight into the mechanism of alternating copolymerizations of diene-dienophile systems and the relationship between the copolymerization and Diels-Alder reaction, we have investigated the copolymerization of electron-rich dienes with acrylonitrile, and report the results in this communication.

EXPERIMENTAL

Monomer Synthesis

1-Ethoxy-1,3-butadiene was synthesized by acid-catalyzed dealcoholation of 1,1,3-triethoxybutane [22]. 1,1,3-Triethoxybutane was prepared from crotonaldehyde and pertinent alcohols by the method of Flaig [23]. 1-Diethylamino-1,3-butadiene was synthesized from crotonaldehyde and diethylamine by the method of Hunig [24].

Copolymer Synthesis

Pyrex polymerization tubes were charged with the prescribed quantities of freshly purified monomers, initiator (AIBN), and benzene as the solvent. The tubes were connected to a high-vacuum line, degassed by several freeze-pump-thaw cycles, and sealed off under vacuum. The monomers were polymerized by heating the sealed tubes at 60°C in a shaking water bath. At the end of the reaction time, the tubes were removed from the bath, cooled to -78°C in a Dry Ice-isopropanol cooling bath in order to stop the reaction, and opened. The solution was then slowly added to a large amount of rapidly stirred petroleum ether. The copolymers were purified by dissolving them in acetone and then precipitating from petroleum ether. After having been dried overnight in vacuum, the copolymers were weighed and analyzed.

RESULTS AND DISCUSSION

The copolymerizations of 1-ethoxy-1,3-butadiene (EBD) and 1-diethylamino-1,3-butadiene (DABD) with acrylonitrile (AN) were carried out by free-radical or spontaneous initiation in benzene at 60°C. In addition to the resulting copolymers, appreciable amounts of Diels-Alder adducts were formed as by-products. The reaction conditions and results are shown in Tables 1 and 2.

In order to determine the reactivity ratios of these systems, the copolymerizations were performed by radical initiation with various monomer feed ratios in benzene at 60°C, with the concentrations of the total monomer and initiator kept constant. The compositions of the resulting copolymers obtained at low conversion were determined by elemental analysis. The results are shown in Tables 3 and 4, respectively. The monomer reactivity ratios r_1 and r_2 were determined by the Fineman-Ross and Kelen-Tüdős methods [25, 26]. The results are summarized in Table 5.

Since the product of the monomer reactivity ratio is much less than unity, the copolymers should have a high degree of alternation of monomer units in the chain.

The formation of constants (K_f) of the AN/EBD and AN/DABD systems were determined by the ^{1}H-NMR method using the equation developed by Foster and Fyfe [27]. The resulting values of K_f were 0.19 at 25°C and 0.10 at 60°C for the AN/EBD system and 0.15 at 25°C for the AN/DABD system.

In the infrared spectra of AN/EBD copolymers, absorptions were seen at

TABLE 1. Conditions for the Copolymerizations of Acrylonitrile with EBD and DABD

Electron-rich diene	m_T,[a] mmol	m_{AIBN},[b] mmol	Volume,[c] mL	Time, h
EBD	27.5	0.099 (0.30%)	4	71
DABD	14.6	0.14 (0.96%)	5	65
EBD	42.5	0	8	70
DABD	36.6	0	4	69

[a] Total monomers.
[b] Moles of AIBN (mol% AIBN based on m_T).
[c] Volume of benzene solvent.

TABLE 2. Yields and Analytical Data for Copolymers in Table 1

Yield, g	Yield, %	Analysis C, %	Analysis H, %	Analysis N, %	F_A[a]	[η], dL/g
0.95	37.9	71.6	8.7	9.2	0.498	0.155[b]
0.10	7.7	73.6	10.2	15.5	0.485	0.459[c]
0.40	12.5	70.6	8.6	8.7	0.477	

[a] Mole fraction of acceptor in the copolymer calculated from the results of elemental analysis.

[b] Intrinsic viscosity in toluene at 25°C.

[c] Intrinsic viscosity in tetrahydrofuran at 25°C.

TABLE 3. Conditions, Yields, and Analytical Data for the Copolymerization of AN with EBD[a]

		Copolymer produced		
EBD in feed, mol%	Time, h	Yield, %	Nitrogen analysis, %	EBD, mol%
27.7	4	7.3	9.4	49.6
37.9	7	10.0	9.2	50.2
50.3	32	18.2	9.1	50.6
63.1	40	10.4	8.6	52.7
73.3	52	9.4	8.3	54.0
83.5	90	5.6	7.5	57.5

[a] Total monomer and initiator concentrations were kept constant at 5500 and 13 mmol/l, respectively.

TABLE 4. Conditions, Yields, and Analytical Data for the Copolymerization of AN with DABD[a]

		Copolymer produced				
			Analysis			
DABD in feed, mol%	Time, h	Yield, %	C, %	H, %	N, %	DABD, mol%
23.3	9	6.1	72.1	9.0	18.3	32.4
27.9	15	6.0	71.7	9.0	18.2	33.0
34.3	20	5.9	72.6	9.2	17.8	35.9
41.2	22	5.3	7.19	9.8	16.6	43.5
49.9	45	7.4	73.4	10.0	15.7	50.2
59.0	62	2.7	73.1	10.6	15.1	55.6

[a] Total monomer and initiator concentrations were kept constant at 5800 and 14 mmol/L, respectively.

TABLE 5. Monomer Reactivity Ratios for the Free-Radical-Initiated Copolymerizations of AN/EBD and AN/DABD

	AN/EBD		AN/DABD	
Calculation method	r_1(EBD)	r_2(AN)	r_1(DABD)	r_2(AN)
Fineman-Ross	0.07	0.03	0.49	0.52
Kelen-Tüdős	0.07	0.02	0.44	0.49

729, 754, 938, and 972 cm^{-1}, which are characteristic of *cis*-3,4, *cis*-1,4, *trans*-3,4, and *trans*-1,4 structures, respectively. In the infrared spectra of AN/DABD copolymers, absorptions were seen only at 730 and 940 cm^{-1}, which are characteristic of *cis* and *trans*-3,4 structures, respectively. The ^{1}H- and ^{13}C-NMR spectra of 1:1 molar ratio AN/EBD and AN/DABD copolymer are shown in Figs. 1 and 2, respectively.

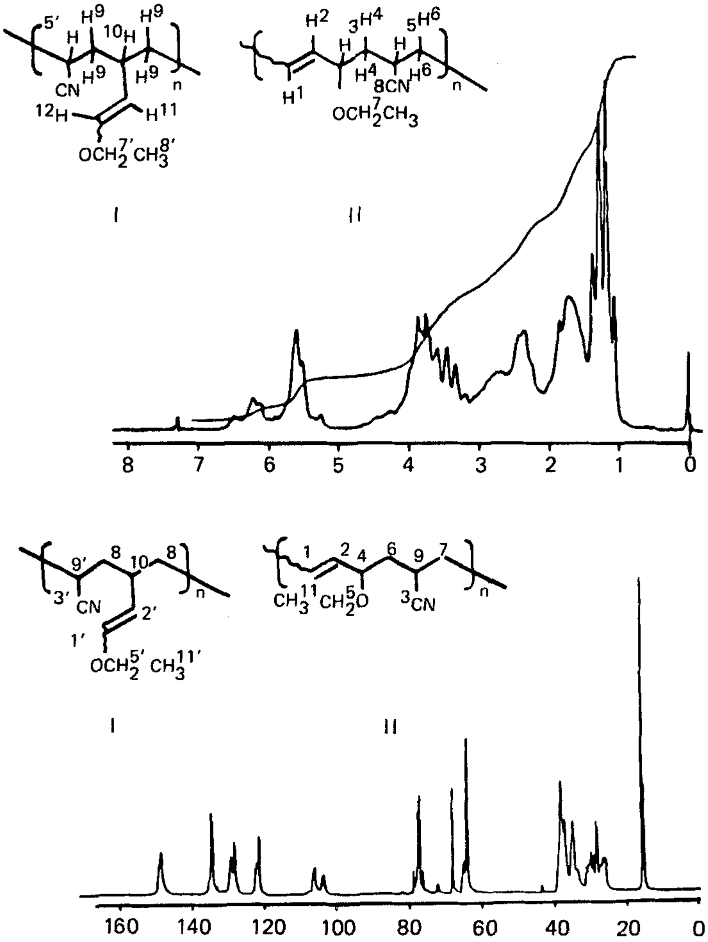


FIG. 1. ^1H-NMR and ^{13}C-NMR spectra of AN/EBD copolymers in $CDCl_3$ at 25°C.

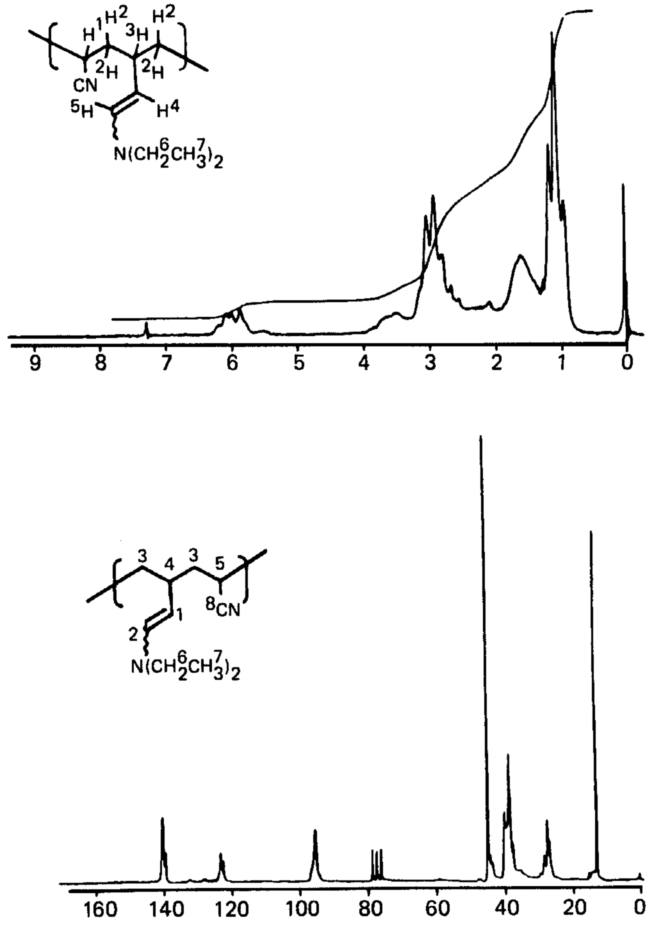
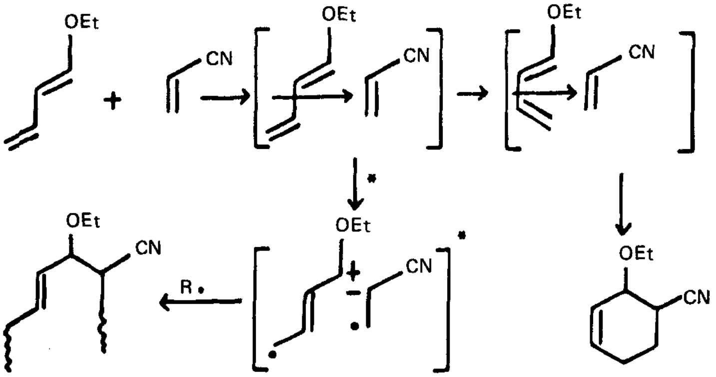


FIG. 2. ^{1}H-NMR and ^{13}C-NMR spectra of AN/DABD copolymers in $CDCl_3$ at 25°C.

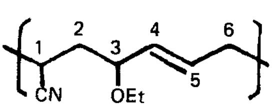


SCHEME 1. Reaction pathway via the complex mechanism.

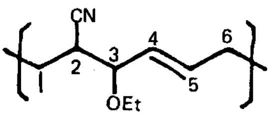
It is proposed that alternating copolymers may result from homopolymerization of electron donor-acceptor complexes generated by the interaction of electron donor monomers with electron acceptor monomers. The reaction scheme, according to this postulation, for these systems is as shown in Scheme 1. The regioselectivity of the cycloaddition reaction was successfully explained by the frontier orbital theory [28, 29].

Another reaction scheme in accordance with the free monomer mechanism is shown in Scheme 2.

There are two possible polymer sequence structures for the *trans*-1,4 addition in the repeating unit of the AN/EBD copolymer. Structure I would be predicted to be formed by the free monomer mechanism, and Structure II sould be predicted to be formed by the complex mechanism:

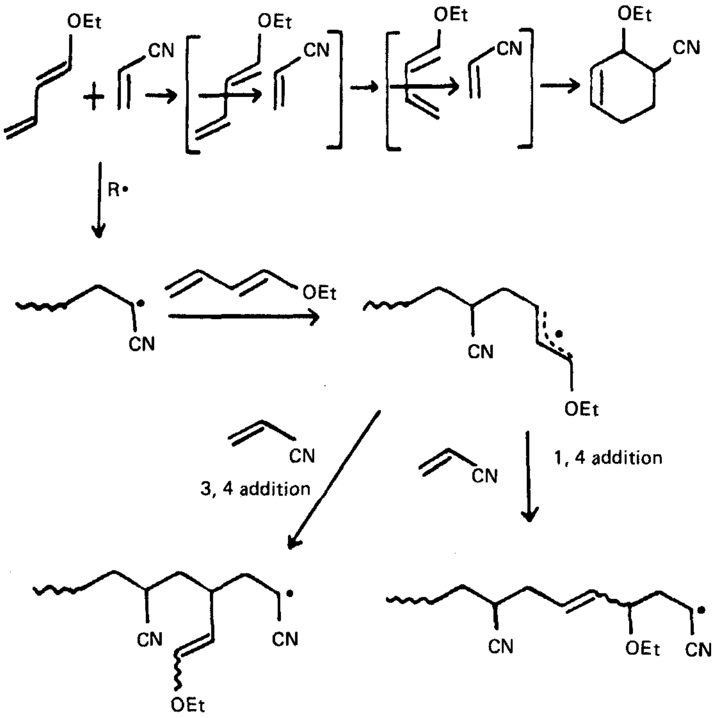


Structure I (head - to - tail)



Structure II (head - to - head)

Both ^{1}H-NMR and ^{13}C-NMR spectra may provide evidence in favor of one of these two structures. To clarify this point, the proton chemical shifts of both sequence structures were calculated [30]. Judging from the chemical shifts and integrations, Structure I was shown to be the preferred sequence



SCHEME 2. Reaction pathway via the free monomer mechanism.

unit in the alternating copolymer. On the other hand, if Structure II had been the real sequence unit in the chemical shift range 1.43-2.06, integration should have shown four protons instead of the three protons actually observed in the spectrum. By using the ^{13}C-NMR spectrum of acrylonitrile/butadiene alternating copolymer [31] as a model compound, the carbon chemical shifts of both sequence structures were calculated [30]. A peak of the methine carbon (2) should appear at δ36.1 and a peak of the methylene carbon (1) should appear at δ30.0 for Structure II. However, the spectrum obtained by the INEPT technique showed that there was no methylene carbon peak in the range of δ24-32, and no methine carbon peak in the range of δ34-40 either. Therefore, the evidence favors Structure I as the true sequence unit in the alternating copolymer, and propagation by the free monomer mechanism probably predominates under the conditions employed.

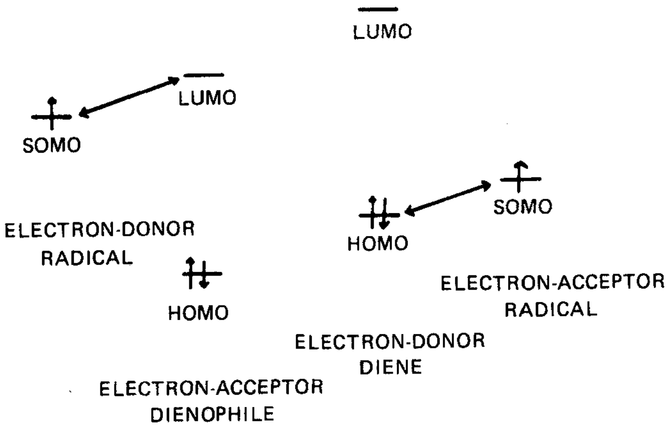


FIG. 3. Frontier orbital energy-level diagram.

It was found that the AN/EBD alternating copolymer could be formed without any free radical catalyst, but no copolymer could be prepared in the presence of a radical inhibitor. So the donor-acceptor interaction in this system probably forms a reactive intermediate of free radical nature to initiate polymerization.

The relative activity of the AN/EBD comonomer pair in radical alternating copolymerization can be discussed qualitatively in terms of frontier orbitals. The frontier orbital energy-level diagram is shown in Fig. 3.

It should be expected that the donor-acceptor interaction between the growing radicals and monomers would significantly reduce their activation energies for transition state formation. Radicals with a higher-energy SOMO will react fast with a substrate with a low-energy LUMO, and radicals with a lower-energy SOMO will react fast with a substrate with a high-energy HOMO.

These considerations may successfully explain the alternating character of the radical AN/EBD copolymerization. The growing radical EBD$^\bullet$ is adjacent to an oxygen atom, thus it has a high-energy SOMO. It reacts faster with a molecule (AN) with a lower-energy LUMO. On the other hand, the growing radial AN$^\bullet$ is adjacent to a nitrile group, which acts as an electron-withdrawing substituent. Thus this radical has a low-energy SOMO, and it reacts faster with a molecule (EBD) with a higher-energy HOMO.

According to the carbon chemical shifts in the ^{13}C-NMR spectra of EBD, electron densities of C2 and C4 are larger than those of C1 and C3. In addition to the steric factor, the growing radical AN˙ should attack at C4 of molecule EBD. This explanation is in good agreement with the structure of the resulting copolymer which consists of *trans*-1,4, *cis*-1,4, *trans*-3,4, and *cis*-3,4 structures.

The relative reactivity of the AN/DABD comonomer pair in radical alternating copolymerization may also be explained qualitatively in terms of frontier orbitals. No *trans*-1,4 and *cis*-1,4 structures were formed; that may be attributed to the steric factor, i.e., the diethylamino group on the C1 position of DABD is bulkier than the ethoxy group on the C1 position of EBD.

SUMMARY AND CONCLUSIONS

In the copolymerization of electron donor dienes and acrylonitrile (AN), the resulting copolymers were found to have equimolar composition by elemental analysis.

The formation constants of the AN/EBD and AN/DABD systems were determined by the NMR method. The values of these constants were so small that the association between the comonomers appear to be weak. Judging from the fact that the products of the monomer reactivity ratios are close to zero, these systems should have a high degree of alternation of monomer units in the equimolar copolymers.

On the basis of ^{1}H-NMR and ^{13}C-NMR spectra, these copolymers were shown to have highly alternating sequence structure. Also, as judged from the chemical shifts, the copolymers were mainly composed of head-to-tail sequence units. These observations suggest that the propagation steps of these systems proceed by the free-monomer mechanism under the conditions studied.

These experimental results, such as the prevalence of head-to-tail configuration and the alternation tendency in the copolymers, can be successfully explained by the frontier orbital theory.

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REFERENCES

[1] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc., 71,* 2703 (1949).

[2] R. S. Mulliken, *J. Phys. Chem., 56,* 801 (1952).

[3] R. S. Mulliken and W. B. Person, *Molecular Complexes; A Lecture and Reprint Volume,* Wiley-Interscience, New York, 1969.

[4] M. J. S. Dewar, *J. Am. Chem. Soc., 74,* 3357 (1952).

[5] K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys., 20,* 722 (1952).

[6] G. B. Butler, K. G. Olson, and C. L. Tu, *Macromolecules, 17,* 1884 (1984).

[7] P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc., 68,* 1495 (1946).

[8] G. B. Butler and K. C. Joyce, *J. Polym. Sci., Part C, 22,* 45 (1968).

[9] G. B. Butler and A. F. Campus, *J. Polym. Sci., Part A-1, 8,* 545 (1970).

[10] G. B. Butler and Y. A. Ragab, *J. Polym. Sci., Polym. Lett. Ed., 14,* 273 (1976).

[11] G. B. Butler and Y. A. Ragab, *J. Polym. Sci., Polym. Chem. Ed., 19,* 1175 (1981).

[12] C. Caze and C. Loucheux, *J. Macromol. Sci.–Chem., A9,* 29 (1975).

[13] E. J. Goethals, A. Cardon, and R. Grosjean, *Ibid., A7,* 1265 (1973).

[14] S. Iwatsuki and Y. Yamashita, *Makromol. Chem., 89,* 205 (1965).

[15] T. Kokubo, S. Iwatsuki, and Y. Yamashita, *Ibid., 123,* 256 (1969).

[16] N. G. Gaylord, M. Stolka, A. Takahashi, and S. Maiti, *J. Macromol. Sci.–Chem., A5,* 867 (1971).

[17] N. G. Gaylord, M. Stolka, and B. K. Patnaik, *Ibid., A6,* 1435 (1972).

[18] C. Walling, E. Briggs, K. Wolfstirn, and F. R. Mayo, *J. Am. Chem. Soc., 70,* 1537 (1948).

[19] Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, *Macromolecules, 7,* 4 (1974).

[20] E. Tsuchida and T. Tomono, *Makromol. Chem., 141,* 265 (1971).

[21] N. G. Gaylord, O. Solomon, M. Stolka, and B. K. Patnaik, *J. Macromol. Sci.–Chem., A8,* 981 (1974).

[22] W. Flaig, *Reichsamt Wirtschaftsausbau, Chem. Ber.,* 093(PB52020), 1073 (1942).

[23] J. Fueno, T. Tsunetsugu, K. Arimoto, and J. Furukawa, *J. Polym. Sci., Part A-1, 9,* 163 (1971).

[24] S. Hunig and H. Kahanek, *Chem. Ber., 90,* 238 (1957).

[25] M. Fineman and S. D. Ross, *J. Polym. Sci., 5,* 529 (1950).

[26] T. Kelen and F. Tüdős, *J. Macromol. Sci.–Chem., A9,* 1 (1975).

[27] R. Foster and C. A. Fyfe, *Trans. Faraday Soc., 61,* 1626 (1965).

[28] I. Fleming, *Frontier Orbital and Organic Chemical Reaction,* Wiley, London, 1976.

[29] M. Blain, S. Odiot, G. J. Martin, J. P. Gouesnard, and O. Chalvet, *Tetrahedron, 36,* 2775 (1980).

[30] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds,* 4th ed., Wiley, New York, 1981.

[31] G. Gatti and A. Carbonaro, *Makromol. Chem., 175,* 1627 (1974).

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