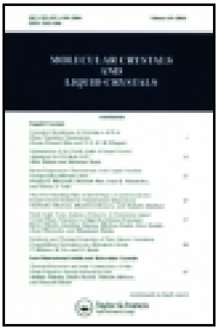

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POLYMERIZATION REACTIONS INVOLVING CHARGE-TRANSFER PHENOMENA

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Abstract Polymerization reactions involving the phenomena of charge-transfer are discussed which include thermally and photochemiclly induced charge-transfer polymerizations, 1:1 alternating radical copolymerizations and electrolytic polymerizations.

INTRODUCTION

Reactions of the electron donor - acceptor system where monomers constitute one or both components often lead to polymerizations either thermally or photochemically.[1] These polymerizations, which proceed via charge-transfer interactions without any added initiator and have been conventionally termed charge-transfer polymerizations, have attracted great attention as involving novel types of initiation. Another class of polymerization that involves charge-transfer interactions is either spontaneously initiated or free radical initiated 1:1 alternating radical copolymerization of an electron donor monomer with an electron acceptor monomer. 1:1 Alternating radical copolymerizations, where charge-transfer complexes formed between monomer pairs may participate in the propagation process of the polymerization, have received attention from both synthetic and mechanistic interest.

We have investigated polymerization reactions involving the phenomena of charge-transfer, i.e., thermally and photochemically induced charge-transfer polymerizations,[1-22] and 1:1 alternating radical copolymerizations,[23-32] in order to elucidate the mechanism and the nature of these polymerization reactions. Electrolytic polymerizations of vinyl monomers have also been studied in view of the preparation of electrically conducting polymers.[33] This paper describes the results obtained with regard to these polymerization reactions.

THERMALLY INDUCED CHARGE-TRANSFER POLYMERIZATION OF N-VINYLCARBAZOLE

It was reported that N-vinylcarbazole (VCZ) is spontaneously polymerized via the formation of charge-transfer complexes in the presence of various electron acceptors.[34,35] In order to elucidate the mechanism of this novel type of polymerization, we have studied the systems such as VCZ - chloranil (CA), VCZ - bromanil (BA), VCZ - fumaronitrile (FN) etc.

It has been found that the rapid polymerization of VCZ by CA in the literature is initiated by traces of 2-hydroxy-3,5,6-trichloro-p-benzoquinone retained in CA and the rate of the true polymerization of VCZ initiated by CA is very slow in nonpolar solvents.[2,3]

The propagation process of the polymerization of VCZ initiated by CA and BA has been shown to be cationic from copolymerization studies.[5] The use of electron acceptor monomers which are capable of undergoing radical copolymerization with VCZ has directly afforded information on the nature of the propagation process of charge-transfer polymerizations. Thus it has been concluded that the spontaneous homopolymerization of VCZ in the presence of FN or maleic anhydride (MAn) proceeds by a cationic mechanism,[1,8] since a free radical mechanism leads to the formation of 1:1 alternating copolymers.[23-25,32] The analysis of resulting polymers by means of the measurement of their fluorescence spectra has been shown to be a new method for distinguishing cationic and free radical propagation mechanisms.

At early stages of the studies, it was simply suggested that the polymerization is initiated by the monomer cation radical generated by the ionization of charge-transfer complexes. We have proposed that the thermally induced polymerization of VCZ in the VCZ - CA and VCZ - BA systems in benzene, which is characteristic in the concurrent formation of carbazole, is initiated either by a zwitterionic intermediate formed by the reaction of VCZ with CA or BA, or by the hydrogen halide produced via the zwitterion.[4,1] Charge-transfer complexes are involved as primary intermediates in the formation reaction of initiating species.

The result that the rate of the cationic polymerization of VCZ in the VCZ - MAn system in 1,2-dichloroethane is much greater in the presence of 2,2'-azobisisobutyronitrile (AIBN) than in the absence of it has indicated the occurrence of the transformation of free radical species into cationic species by electron transfer.[8]

PHOTOCHEMICALLY INDUCED CHARGE-TRANSFER POLYMERIZATIONS

N-Vinylcarbazole - Electron Acceptor System

We have studied primary processes and follow-up reaction pathways of the photochemical reaction of the VCZ - electron acceptor system, employing a high vacuum system and using various organic electron acceptors, in order to elucidate the nature and the whole picture of the reaction which remained unresolved.

Studies of the effect of the wavelength of the incident light on the polymerization of the VCZ - CA and VCZ - BA systems in benzene have shown that the cationic polymerization of VCZ is initiated both by the selective excitation of a ground state charge-transfer complex and by local excitation of a component molecule.[10,19] The photochemical formation of a transient VCZ cation radical and an electron acceptor anion radical has been demonstrated for the first time by means of flash photolysis for the VCZ - CA system and then for the VCZ - pyromellitic dianhydride (PMDA) system in several solvents.[12,13,18]

The photochemical reaction of the VCZ - electron acceptor system exhibits multireaction courses involving cationic homopolymerization of VCZ, cyclodimerization of VCZ to give trans-1,2-dicarbazol-9-yl cyclobutane, and radical homopolymerization of VCZ or radical copolymerization with an electron acceptor monomer. It has been found that these multireactions are general with many organic electron acceptors except for some electron acceptors that undergo dissociative electron capture, e.g., CBr_4, and that the reaction course is controlled primarily by the basicity, i.e., cation-solvating ability, of the solvent.[11,14,15,17] That is, while cationic polymerization of VCZ proceeds in nonbasic solvents, e.g., benzene, dichloromethane, 1,2-dichloroethane, and nitrobenzene, the cyclodimerization of VCZ takes place exclusively in moderately basic solvents, e.g., acetone, methyl ethyl ketone, methanol, and acetonitrile. In stronger basic solvents, e.g., N-methyl-2-pyrrolidinone, N,N-dimethylformamide, and dimethyl sulfoxide, both the cyclodimerization and radical polymerization of VCZ take place simultaneously, the radical polymerization being increasingly favored over the cyclodimerization with an increase in the solvent basicity. In the strongest basic solvent examined, hexamethylphosphoric triamide, only radical polymerization of VCZ occurs. When an electron acceptor monomer, e.g., FN or diethyl fumarate (DEF), is used, free radical homopolymerization of VCZ which proceeds in stronger basic solvents is replaced by the radical copolymerization of VCZ with the electron acceptor monomer. In the VCZ - electron acceptor monomer (FN, DEF, MAn) system, cationic homopolymerization of VCZ in benzene and the cyclodimerization of VCZ in moderately basic solvents are accompanied by radical copolymerization.[14,15]

These multireactions and the solvent control of the reaction course have been explained in terms of cation solvation of the VCZ cation radical and the resulting VCZ dimer cation radical intermediates.[1,11,14,15,17]

It has been found that the photochemical reaction of VCZ alone in a solution in the presence of oxygen entirely differs from that under high vacuum.[9,16] Typically, while inefficient free radical polymerization of VCZ proceeds in acetone under high vacuum, the cyclodimerization of VCZ takes place preferentially in acetone in the presence of dissolved oxygen. The features of the photochemical reaction of the VCZ - oxygen system in polar solvents are essentially the same as those of the VCZ - organic electron acceptor system under high vacuum. It has been indicated that electron transfer occurs from VCZ in the electronically excited state to oxygen in polar solvents to give the VCZ cation radical and superoxide. It has also been found that photocationic polymerization of VCZ occurs in dichloromethane and 1,2-dichloroethane even in the absence of oxygen or any added electron acceptor, whereas direct irradiation of VCZ alone in e.g., acetone or DMF under high vacuum leads to inefficient radical polymerization. It has been suggested that the solvents, dichloromethane and 1,2-dichloroethane, act as electron acceptors.[16,1]

N-Vinylcarbazole - Electron Donor (Amine) System

We have studied the photochemical reaction of the VCZ - amine system where the electron donating VCZ monomer may act as an electron acceptor in the electronically excited state. It has been found that photoradical polymerization of VCZ is induced in benzene and greatly accelerated in acetone in the presence of amines such as triethylamine, tri-n-propylamine, and N,N-diethylaniline.[20] It is suggested that the VCZ - N,N-diethylaniline system in acetone involves electron transfer to generate the VCZ anion radical and the amine cation radical, followed by proton transfer to give neutral radical species, which initiate radical polymerization of VCZ.[21]

2-Vinylnaphthalene - Fumaronitrile System

While the photochemical reaction of the VCZ - electron acceptor monomer (FN, DEF, and MAn) system in benzene leads to cationic homopolymerization of VCZ accompanied by radical copolymerization of VCZ with the electron acceptor monomer, the photochemical reaction of the 2-vinylnaphthalene (VN) - FN system in benzene has been shown to yield a VN-FN copolymer and VN cyclodimers, 1,2,3,4-tetrahydro-4-(2-naphthyl)phenanthrene and trans-1,2-di(2-naphthyl)cyclobutane probably via ion radical intermediates. By contrast, the benzophenone-sensitized reaction of the VN - FN system in benzene produces four isomeric VN-FN cycloadducts as main products together with minor amounts of trans- and cis-cyclobutane cyclodimers via the triplet state of VN.[22]

2-Vinylnaphthalene - Amine System.

In contrast to photopolymerization of VCZ in a high vacuum system, direct irradiation of VN produces cis- and trans-1,2-di(2-naphthyl)cyclobutane as main products.[36]

We have studied the effect of charge-transfer interactions on the photochemical reaction of VN. It has been found that charge-transfer interactions between VN in the excited singlet state and amines (triethylamine, DABCO) in the ground state significantly alter the product distribution in the photochemical reaction of VN in benzene, increasing the trans/cis ratio of the cyclodimer from 0.1 in the absence of amines to ca. 2.0 in the presence of DABCO. Based on the results of triplet quenching and triplet sensitization experiments, it has been indicated that charge-transfer interactions between VN in the excited singlet state and the amines in the ground state quench the reaction via the VN singlet state that gives cis-cyclodimer, enhancing deactivation to its ground state and population of the VN triplet state which favors the formation of the trans-cyclodimer.[36] On the other hand, the photochemical reaction of the VN - triethylamine system in acetonitrile yields ethylnaphthalene, 2,3-di(2-naphthyl)butane, and the VN-amine adduct via the VN anion radical and amine cation radical.

1:1 ALTERNATING RADICAL COPOLYMERIZATIONS

New 1:1 Alternating Radical Copolymerization Systems

It is known that certain systems consisting of electron donor monomers and electron acceptor monomers undergo free radical copolymerizations to yield 1:1 alternating copolymers.

We have found that VCZ is copolymerized with electron acceptor monomers such as fumaronitrile (FN), diethyl fumarate (DEF) and maleic anhydride (MAn) under a free radical initiation to yield 1:1 alternating copolymers regardless of the monomer feed composition.[23-25,32] Vinyl ferrocene also produces 1:1 alternating copolymers with FN and DEF irrespective of the monomer feed composition.[28,31]

The AIBN-initiated polymerization of the VCZ - MAn system involves both cationic homopolymerization of VCZ and 1:1 alternating radical copolymerization of VCZ with MAn. It has been found that the polarity and basicity of solvents greatly affect the ratio of the competing cationic homopolymerization of VCZ to the 1:1 alternating radical copolymerization.[32,8] That is, the polymerization in a nonpolar, basic solvent, dioxane, produces predominantly the 1:1 alternating copolymer, whereas the polymerization in a polar, nonbasic solvent, 1,2-dichloroethane, yields almost exclusively VCZ homopolymer by a cationic mechanism. In a nonpolar, nonbasic solvent, benzene, the ratio of the VCZ homopolymer to the 1:1 alternating copolymer varies depending upon the monomer feed composition.

Mechanism for the 1:1 Alternating Copolymerization

Generally 1:1 alternating radical copolymerization systems involve the formation of a weak charge-transfer complex between monomer pairs. The propagation mechanism for the 1:1 alternating copolymerization has long been a subject of controversy. Two different mechanisms were proposed which include homopolymerization of a charge-transfer complex formed between monomer pairs (charge-transfer complex monomer) and cross-reactions of free monomers. However, both mechanisms are not capable of explaining satisfactorily polymerization features of 1:1 alternating radical copolymerization.[25,30]

We have proposed a generalized propagation mechanism for the 1:1 alternating radical copolymerization, which consists of cross-reactions of both free monomers and the charge-transfer complex monomer on the basis of the viewpoint that 1:1 alternation is brought about by the stabilization of the transition state of the cross-reactions relative to homoreactions.[25]

$$\begin{array}{lcll}
m_1\cdot & + & M_2 & \xrightarrow{k_{12}} m_2\cdot \\
m_2\cdot & + & M_1 & \xrightarrow{k_{21}} m_1\cdot \\
m_1\cdot & + & M_2M_1 & \xrightarrow{k_{1c}} m_1\cdot \\
m_2\cdot & + & M_1M_2 & \xrightarrow{k_{2c}} m_2\cdot
\end{array}$$

Based on this mechanism, we have developed a method for quantifying the contribution of the free monomer and the charge-transfer complex monomer to the polymerization rate by analyzing the overall initial copolymerization rate as a function of the total monomer concentration under each fixed monomer feed composition.[29,30] In the case of bimolecular termination, the overall initial copolymerization rate Rp is

$$R_p = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[M_1]^2 + A(X)[M_1] \qquad (1)$$

$$R_p(f) = A(X)[M_1] \qquad (2)$$

$$R_p(CT) = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[M_1]^2 \qquad (3)$$

$$A(X) = \frac{2k_{21}k_{12}R_i^{1/2}X}{\{k_{t11}k_{21}{}^2 + 2k_{t12}k_{21}k_{12}X + k_{t22}k_{12}{}^2X^2\}^{1/2}}$$

$$(R = 2k_d f[I])$$

$$[M_2] = X[M_1]$$

$$R_p/[M_1] = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2C}}{k_{21}}X\right)[M_1] + A(X) \qquad (4)$$

expressed by Eq. (1), which is a superposition of the reaction rates of free monomers Rp(f) (Eq. (2)) and of the charge-transfer complex monomer Rp(CT) (Eq. (3)). If the proposed mechanism holds, the plot of $Rp/[M_1]$ vs. $[M_1]$ for Eq. (4), which is derived from Eq. (1), should be linear for each given monomer feed ratio X.

The method has been applied to the VCZ - DEF, VCZ - FN, vinylferrocene - DEF, and vinylferrocene - FN 1:1 alternating copolymerization systems.[30,31] The results show that the plot for Eq. (4) is linear, having definite values of a slope and an intercept, for each given X in all the systems examined. As a result, the degree of the participation of free monomers and the charge-transfer complex monomer has been quantified for the above 1:1 alternating radical copolymerization systems. It has been shown that the free monomer contributes to the polymerization rate to a much greater extent than the charge-transfer complex monomer in both VCZ - DEF and VCZ - FN systems and that the degree of participation of each of them varies depending on the total monomer concentration and on the monomer feed ratio.[30]

ELECTROLYTIC POLYMERIZATION OF N-VINYLCARBAZOLE

It has been shown that the controlled-potential anodic oxidation of VCZ in dichloromethane with tetra-n-butylammonium perchlorate as the supporting electrolyte deposits an electrically conducting polymer on the surface of the electrode.[33] The polymer formed is poly(N-vinylcarbazole) electrochemically doped with ClO_4^-, the structure of which is cross-linked at the 3- and/or 6- position of the carbazole ring. The polymer exhibits a room temperature conductivity of ca. 1×10^{-6} S cm^{-1}. Electrochemical doping of poly(N-vinylcarbazole) (PVCz) and substituted PVCz transforms them into conducting polymers with room temperature conductivities up to 6 x 10^{-4} S cm^{-1}.[37]

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