Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Ionic Polymerization of Vinyl Aromatic Monomers

James M. Pearson[a]
[a] Research Laboratories Xerox Corporation Webster, New York

To cite this Article Pearson, James M.(1975) 'Ionic Polymerization of Vinyl Aromatic Monomers', Journal of Macromolecular Science, Part A, 9: 6, 1029 — 1046

To link to this Article: DOI: 10.1080/00222337508081506

URL: http://dx.doi.org/10.1080/00222337508081506

J. MACROMOL. SCI.—CHEM., A9(6), pp. 1029-1046 (1975)

Ionic Polymerization of Vinyl Aromatic Monomers

JAMES M. PEARSON

Research Laboratories
Xerox Corporation
Webster, New York 14580

ABSTRACT

The ionic polymerization of vinyl monomers possessing aromatic and heterocyclic functional groups has not been studied in any systematic fashion. Only in a few isolated cases have detailed mechanistic and structural studies been reported. The anionic polymerization of a number of vinylanthracene monomers has recently been investigated and some rationalization of this system is presented. The cationic and anionic polymerization of the N-, 3-, and 2-vinylcarbazole series of monomers is discussed in some detail. The important role of vinyl aromatic/vinyl heterocyclic monomers, i.e., diphenylethylene and the vinylcarbazoles, in elucidating the mechanistic aspects of cationic polymerization, "change transfer" polymerization, and photoionic polymerization is considered.

INTRODUCTION

Using the refined synthetic and analytical tools available today, the organic chemist possesses the capability for introducing virtually any functional group into a vinyl monomer. An even greater challenge, perhaps, is the polymerization of such monomers into high molecular weight polymers and copolymers. Within the class of monomers covered here, i.e., vinyl aromatics/heterocyclics, free radical polymerization methods often give rise to low molecular weight, poorly defined products resulting from facile reactions of the nonselective free radicals with the functional groups present in the system. In certain cases, ionic polymerization procedures provide the only route to the desired polymeric products.

Polymeric materials possessing aromatic (i.e., naphthalene, anthracene, pyrene) and heterocyclic (i.e., indole, carbazole, phenothiazine) groups have not found widespread commercial utility. These are specialty monomers/polymers, and it is as specialty materials that they are finding and will continue to find applications, i.e., organic semiconductors/photoconductors, polymer stabilizers/destabilizers, photoreactive materials, and in pharmacological and medical areas. It is perhaps for this reason that no systematic studies of the ionic polymerization of these monomers have been reported. The effect of aromatic ring structure and of heterogroups on the polymerization reactions have been elucidated only in a few isolated cases.

It is only possible here to select in a subjective manner and review some of the more novel and interesting systems and to speculate on the future trends of this area of ionic polymerization. I would like to emphasize the need to consider the chemical, material, and mechanistic aspects of polymerization processes, but unfortunately few systems have been subjected to such detailed analyses.

The pioneering and elegant studies of the Syracuse group have established anionic polymerization on a sound base. The kinetic and mechanistic aspects of the polymerization processes are well understood, except in a few isolated cases. The role of solvent, counterion, etc. can be predicted, and it is possible to exercise a high degree of control over most polymerization reactions. The situation is considerably more complicated in the field of cationic polymerization and no unified mechanistic picture has emerged. Here the individual reaction steps are complex and the polymerization is not readily amenable to control. Although living-type polymers have been demonstrated for ring-opening polymerization, i.e., THF, no examples of a living carbenium ion system have yet been found.

ANIONIC POLYMERIZATION

Perhaps one of the most intriguing unsolved problems in this area is the polymerization of 9-vinylanthracene (1). This monomer has yielded only low molecular weight products, $\overline{M}_n \sim 1000$ to 5000, by all known polymerization techniques [1]. The anionic polymerization of the other members of the series, i.e., vinyl naphthalenes, vinyl phenanthrenes, and vinyl pyrene, have all been reported to proceed in a conventional manner.

The anomalous results for 9-vinylanthracene have not been explained. Several plausible mechanisms have been proposed: 1) an extremely efficient chain (electron) transfer process, 2) a through-the-ring propagation, and 3) a "wrong" monomer addition. These are shown in Fig. 1.

The synthesis and the anionic polymerization of 9-vinyl-10-methylanthracene (1a), 2-vinylanthracene (2) and 2-propenyl-2-anthracene (2a) have recently been investigated in our laboratory in an attempt to resolve these issues [2] (Fig. 2).

With the 2-vinylanthracenes it has been possible to achieve high molecular weight, $\overline{M}_n \sim 10^5$ to 10^6, soluble polymers. IR analysis is indicative of a conventional 1,2 vinyl polymer structure with no involvement of the anthracene rings.

The spectra of the propagating anions of monomers 2 and 2a are shown in Figs. 3 and 4, respectively. Identical spectra were obtained

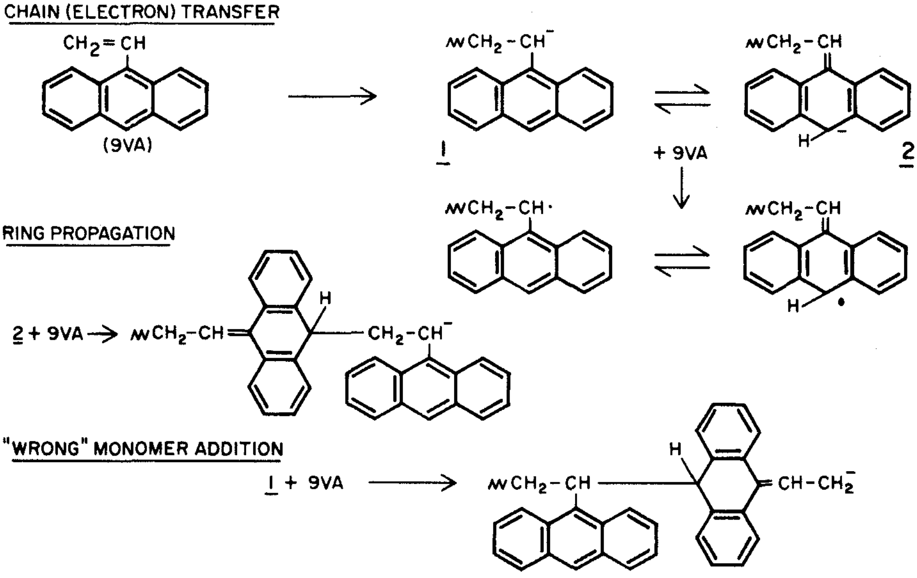


FIG. 1. Anionic polymerization of 9-vinylanthracene.

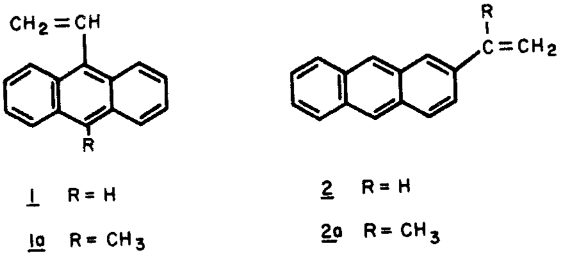


FIG. 2. 9-Vinylanthracene (1), 9-vinyl-10-methylanthracene (1a), 2-vinylanthracene (2), and 2-propenyl-2-anthracene (2a).

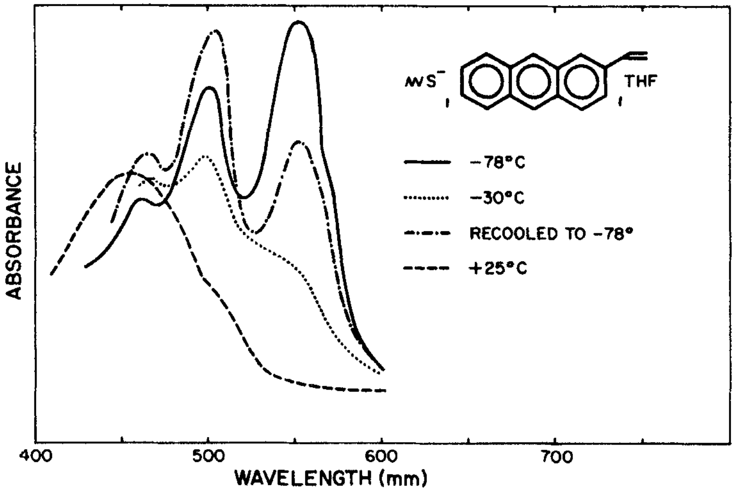


FIG. 3. Optical spectrum of the carbanion formed from 2-vinylanthracene.

from addition of a slight excess of monomer to a living polystyrene solution and from the polymerization reaction. In an attempt to substantiate the structure of this carbanion, the model compound 1-propenyl-2-anthracene was synthesized. The spectrum of the carbanion from this olefin was essentially identical to that from 2-vinylanthracene shown in Fig. 3. All these anions exhibit instability at elevated temperatures, decomposing to give some species with an absorption maxima around 460 nm which is not effective in initiating polymerization.

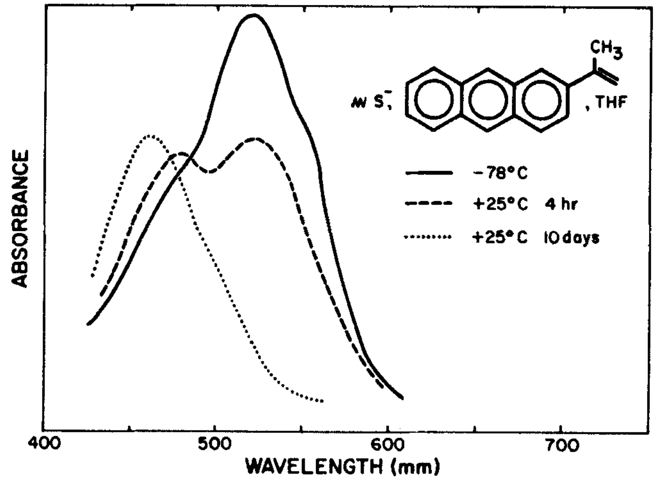


FIG. 4. Optical spectrum of the carbanion formed from 2-propenyl-2-anthracene.

All attempts to duplicate these results for the 9-vinylanthracene monomers were unsuccessful. The spectrum of the species generated by addition of 9-vinylanthracene to living polystyrene at -78°C is shown in Fig. 5 (9-vinyl-10-methylanthracene produces a very similar spectrum), and it exhibits some of the features anticipated for the conventional $\sim CH_2-\underset{A}{CH^-}$ carbanion. The spectrum of the 9-anthrylmethide anion has been reported [3], and Fig. 6 shows the anion formed from the 1-propenyl-9-anthracene model compound. The species produced from the olefins at low temperatures are highly unstable and possibly rearrange to produce the ring-type carbanion. The spectra of the species existing at ambient temperatures are not inconsistent with such a structure, c.f., the adducts formed between the styrene anion and anthracene (~450 nm) pyrene (~500 nm) and benz[e]pyrene (~600 nm) [4].

Although the results from these investigations are not totally definitive, it has been clearly demonstrated that anionic polymerization of 2-vinylanthracene monomers to high molecular weight polymers can be achieved under proper reaction conditions. The 9-vinylanthracene system remains a paradox but the present spectroscopic analysis casts very serious doubts on the reliability of the published work on this monomer.

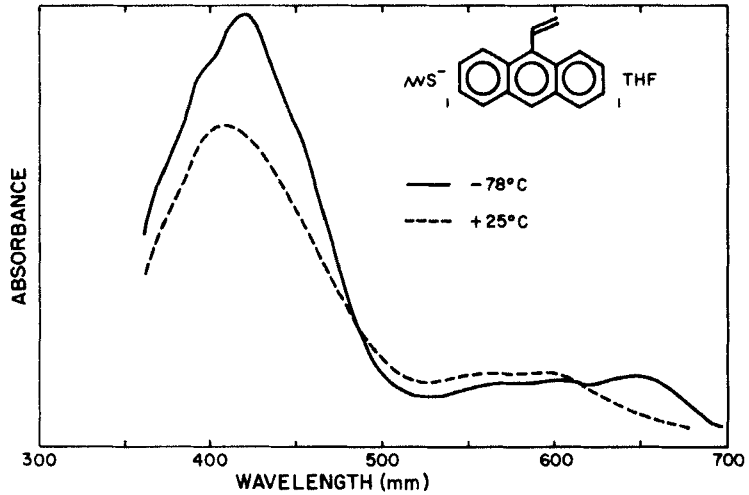


FIG. 5. Optical spectrum of the species formed in the reaction of 9-vinylanthracene with "living" polystyrene in THF.

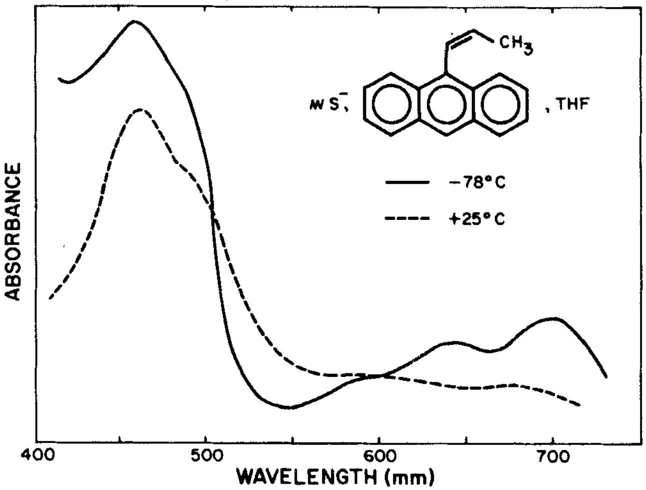


FIG. 6. Optical spectrum of the species formed in the reaction of 1-propenyl-9-anthracene with "living" polystyrene in THF.

These vinylanthracene studies serve to illustrate the complexities resulting from participation of the aromatic moiety in the polymerization reaction. Carbanion addition and electron transfer to the pyrene nucleus was also demonstrated in the copolymerization of 1-vinyl pyrene [5]. The anionic homopolymerization of this monomer exhibited all the characteristics of a "living" polymer system. In the formation of block copolymers, however, anomalous reactions and products were shown to result from the addition and electron transfer processes illustrated by Fig. 7.

Such complications can be used to advantage [6]. The dianionic adducts formed between "living" polymers and aromatic/heterocyclic molecules can be coupled according to the scheme of Fig. 8 using a variety of suitable difunctional reagents. In this case the products are copolymers with the aromatic/heterocyclic moieties incorporated into the polymer backbone.

In the case of vinyl heterocyclic monomers only a few systems have been investigated in enough detail to warrant consideration. A very interesting intramolecular solvation/coordination phenomenon has been found in the polymerization of 2-vinylpyridine and 2-vinylquinoline [7].

The anionic polymerization of N-vinylcarbazole (3) has also been studied [8] and it was concluded that the high electron density at the $>N-CH=CH_2$ site precluded formation of a stable anion. However, we have recently shown [9] that the corresponding 3-vinyl and 2-vinyl-N-alkylcarbazole monomers (4 and 5) could be polymerized anionically (Fig. 9).

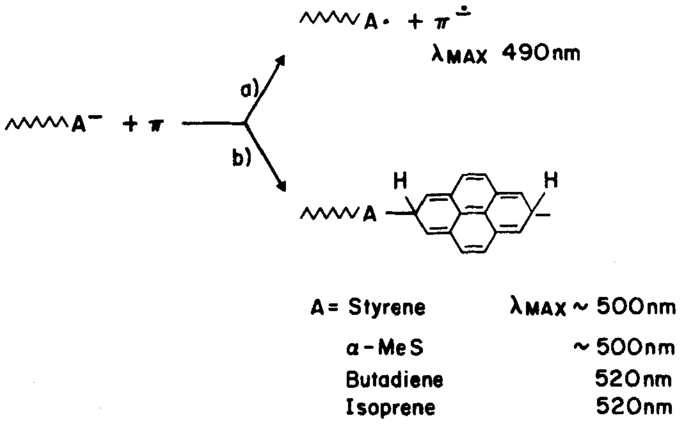


FIG. 7. Reactions of living polymer anions with pyrene.

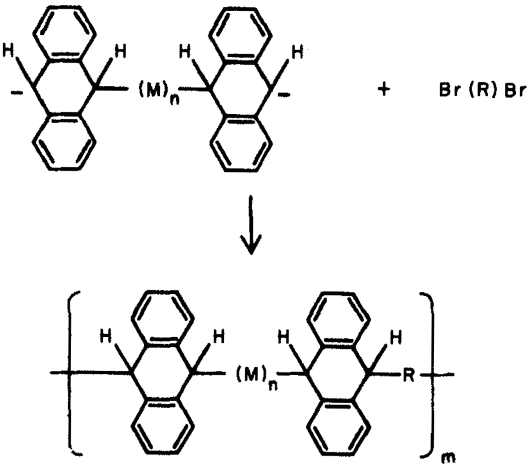
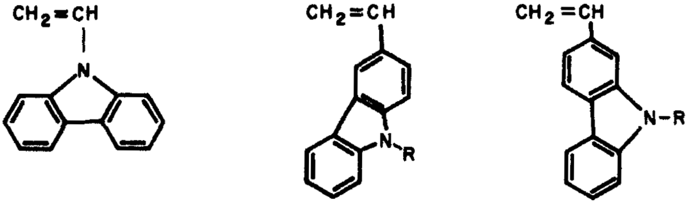


FIG. 8. Copolymer formation via carbanion coupling reactions.



3 4 5

FIG. 9. N-Vinylcarbazole (3), 3-vinyl-N-alkylcarbazole (4), and 2-vinyl-N-alkylcarbazole (5).

The synthesis of the 2-vinyl-N-ethylcarbazole monomer presented an interesting challenge and the reaction sequence of Fig. 10 was developed in our laboratory.

The 2-vinyl monomer exhibits all the features of a "living" polymer system while the 3-vinyl derivative is stable only at low temperatures, $<-50°C$. The absorption spectra of the two polymer anions are shown in Fig. 11; $\sim 2VK^-$, 498 nm, $\epsilon = 1.6 \times 10^4$ and $\sim 3VK^-$, 545 nm, $\epsilon = 1.5 \times 10^4$. Unlike the N-vinyl- and 3-vinylcarbazoles, the vinyl function in 5 is not in direct conjugation with the electron-rich nitrogen moiety and the carbanion is stable enough to effect polymerization. In its

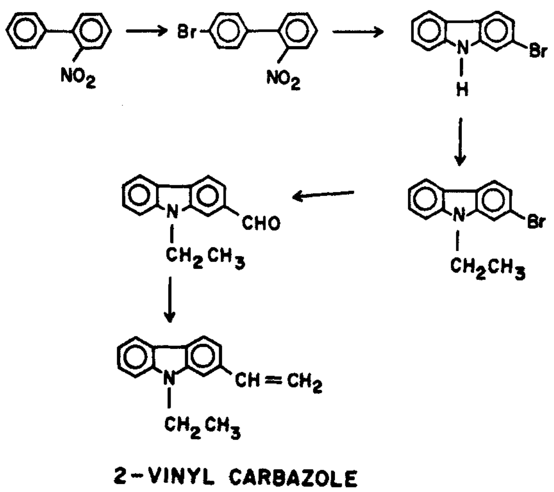


FIG. 10. Synthesis of the 2-vinyl-N-ethylcarbazole monomer.

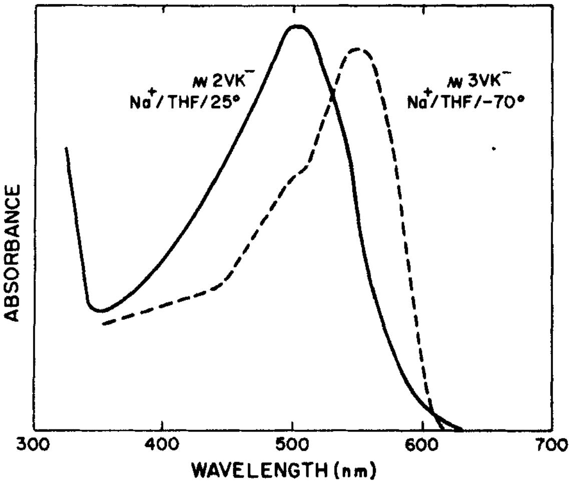
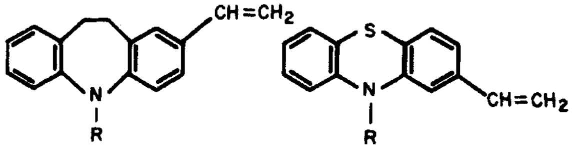


FIG. 11. Optical spectra of the carbanions formed from 2-vinyl-N-ethylcarbazole.



6 7

FIG. 12. N-Methyl-2-vinyliminobibenzyl (6) and N-ethyl-2-vinylphenothiazine (7).

anionic polymerization reactions, 5 behaves like a substituted styrene. The 3-vinyl monomer, 4, exhibits a behavior intermediate between the 2- and N-vinyl systems.

Two other interesting vinyl heterocyclic monomers have recently been shown to polymerize by anionic methods [10], N-methyl-2-vinyliminobibenzyl (6) and N-ethyl-2-vinylphenothiazine (7) (Fig. 12). Here again, as with the 2-vinylcarbazole, the molecular structure inhibits direct conjugation of the vinyl group with the electron-rich center and permits facile, controlled anionic polymerization. Although many other monomers are known [11], there have been no serious studies of the oxygen- or sulfur-containing vinyl heterocyclic monomers.

CATIONIC POLYMERIZATION

There have been very few detailed studies of the cationic polymerization of vinyl aromatic monomers other than styrene and its derivatives which I will exclude here. Virtually all vinyl monomers possessing polynuclear aromatic hydrocarbon groups can be polymerized cationically, but the absence of information on polymer properties and structure in the literature is alarming. The complex structure claimed for the polymer (oligomer) of 9-vinylanthracene [12] shows the complications which can result from unstable and reactive carbenium ions (Fig. 13).

We have recently re-investigated [2] the cationic polymerization of the 9- and 2-vinylanthracene monomers. Polymers with molecular weights around 2 × 10^4, which are readily soluble, were obtained, and spectroscopic analysis favors a conventional 1,2-vinyl polymer structure. These polymerizations were critically dependent on monomer purity, monomer and polymer solubility, and the mechanism is still not completely established.

In the vinyl heterocyclic monomer case the opposite picture is found.

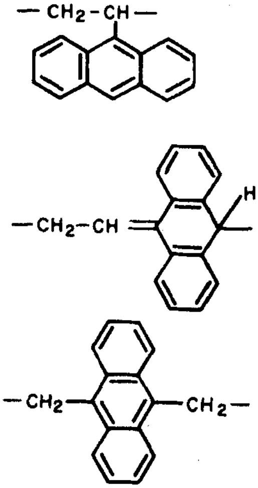


FIG. 13. Structure of poly-9-vinylanthracene.

The monomer N-vinylcarbazole is probably one of the most widely used in cationic polymerization studies. However, here again no systematic studies of variations in the heterocyclic ring structures have been made.

One of the major problems in any cationic polymerization is to establish the nature and the concentration of the active carbenium ion species. Studies with the model vinyl monomer, 1,1-diphenylethylene, where the complications arising from propagation, etc. are precluded, illustrate the complex nature of the initiation reaction.

In methylene chloride as solvent and $SbCl_5$ as initiator, the following reactions can occur [13] (D is 1,1-diphenylethylene, $D^{+\cdot}$ the olefin radical cation, D^{+} the diphenylethyl carbenium ion):

$$D + SbCl_5 \rightleftharpoons [D\ SbCl_5\ \text{complex}] \rightleftharpoons D^{+\cdot}, SbCl_5^{-\cdot} \tag{1}$$

$$2D^{+\cdot}, SbCl_5^{-\cdot} \rightarrow SbCl_5^{-\cdot}, {}^{+}DD^{+}\ SbCl_5^{-\cdot}$$

(electron transfer)

$$D + SbCl_5 \rightarrow ClD^{+}, SbCl_4^{-} \tag{2}$$

(Cl^{+} transfer)

$$\underset{\text{(cocatalyst)}}{D + SbCl_5 + (H_2O)} \rightarrow HD^+, SbCl_5OH^- \qquad (3)$$

The reaction is strongly dependent on the monomer/initiator ratio and on the nature of the initiator; no dimerization was observed using $TiCl_4$ [14]. Further evidence for the electron transfer mode of initiation, i.e., Eq. (1), has been reported using the stable triarylaminium salts, $Ar_3N^{+\cdot}X^-$, as initiators and 1,1-diphenylethylene and N-vinylcarbazole as monomers [15] (Fig. 14).

Clearly, each individual polymerization system has to be considered on its own merits, and it seems unlikely that any general reaction scheme comprising a sequence of elementary reactions (as for free radical and anionic polymerization) can be established.

Investigations of N-vinylcarbazole polymerization initiated with stable carbenium ion salts has provided key insights into the propagation reaction. The pioneering work of the Liverpool group on this system has permitted k_p^+ values to be estimated for the first time [16]; k_p^+ (NVK) ~ 10^5 to 10^6 $mole^{-1}$ l sec^{-1} in the temperature range -25 to 25°C. The mechanism has been well established, e.g., with tropylium ion [16] (Fig. 15).

The role of solvent, counterion, etc., even in this relatively "clean" polymerization system, are still far from being resolved. Parallel studies using the 2- and 3-vinylcarbazole monomers may help clarify some of these outstanding issues.

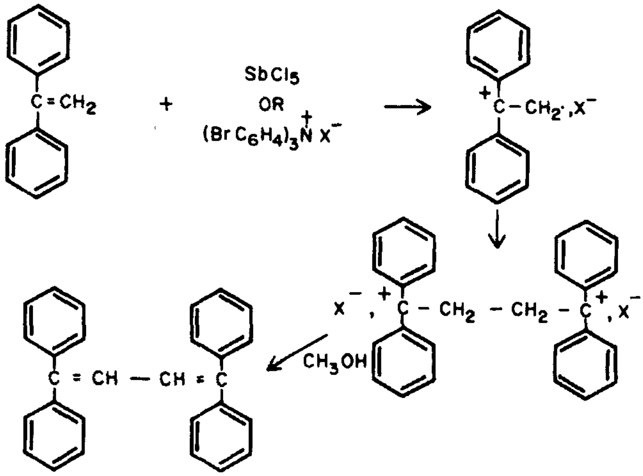


FIG. 14. Electron transfer mode of initiation.

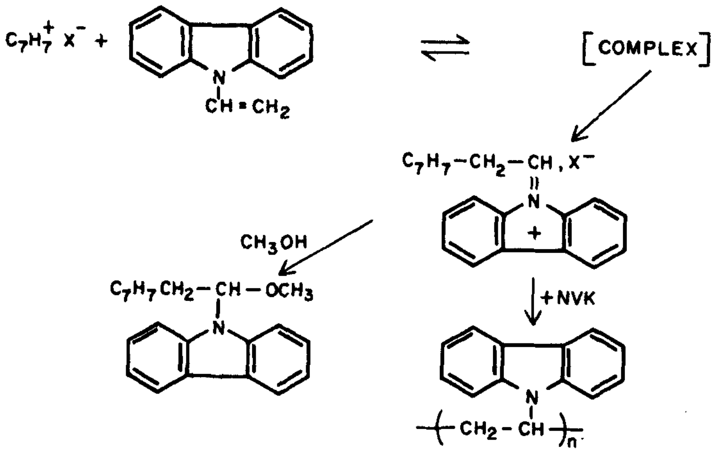


FIG. 15. Addition mode of initiation of cationic polymerization of N-vinylcarbazole.

One of the most extensively studied areas in this field is that of the so-called "charge-transfer" polymerization [17]. In principle, monomers exhibiting donor or acceptor functions should be polymerizable via charge-transfer interaction with a suitable partner. Olefins possessing electron-withdrawing groups are not widely known and few such systems have been characterized. On the other hand, monomers having electron-donor characteristics have been widely investigated and N-vinylcarbazole (NVK) has been a favorite donor monomer with a wide variety of electron acceptors including polymerizable and copolymerizable monomers. In spite of the intensive work with NVK, there is still considerable conflict between various groups. The possible reactions between NVK and typical electron acceptor molecules are summarized in Fig. 16.

The course of the reaction in any particular system will be determined by the solvent, impurities (for example, O_2 and acid), temperature, and activation by light. Too many investigators have failed to appreciate the extreme sensitivity of these systems with the result that the literature is full of conflicting data.

The initiation of cationic polymerization via charge-transfer complexes can be illustrated by the NVK/tetracyanoethylene (TCNE) system. An idealized reaction scheme is presented in Fig. 17.

However, the mechanism of this polymerization has been shown to be considerably more complex [18, 19]. In many instances polymerization results from the acidic impurity tricyanoethenol [20]. Excluding

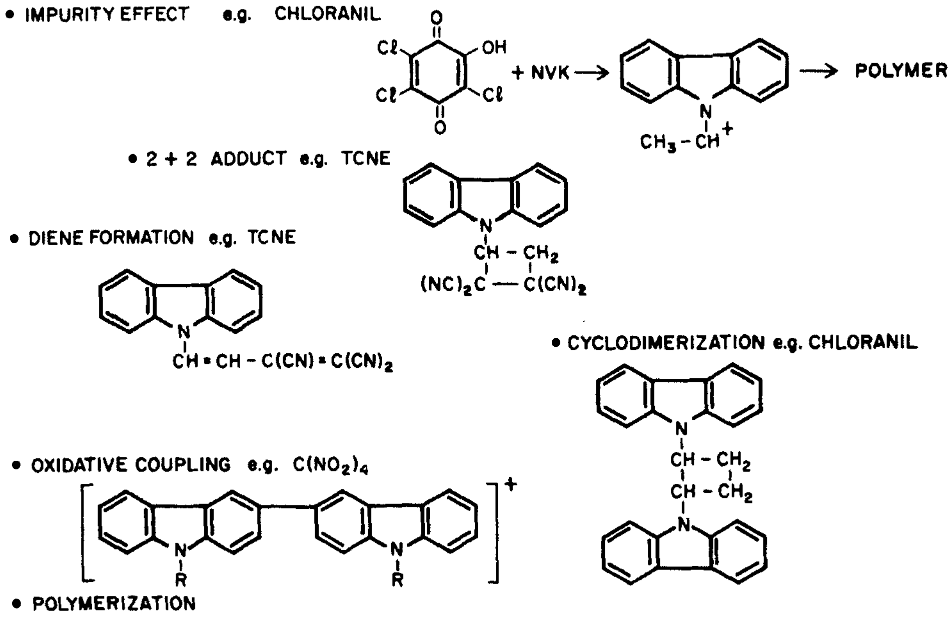


FIG. 16. Reactions between NVK and electron acceptors.

this effect, the reaction scheme of Fig. 18 has been proposed to account for the reaction products found in the NVK/TCNE system.

This is one of the few cases where there is solid evidence to substantiate the formation of olefin cation radicals from thermal activation of charge-transfer complexes. In all too many instances the appearance of charge-transfer absorption bands is taken as evidence for the participation of the complexes and the ion radical products as reaction intermediates.

Photochemical activation of charge-transfer complexes can be utilized to initiate polymerization [21]. It is extremely important to recognize the nature and formation of the various possible excited states. These are described in the scheme illustrated by Fig. 19.

Here, both direct excitation of the ground state complex and interactions between locally excited donor or acceptor with ground state partner are considered. Furthermore, singlet or triplet excited states may be involved in the reactions. There have been numerous studies of the photoinduced reactions of NVK and the chloranil system is perhaps the most clearly understood [22]. Most of the controversial

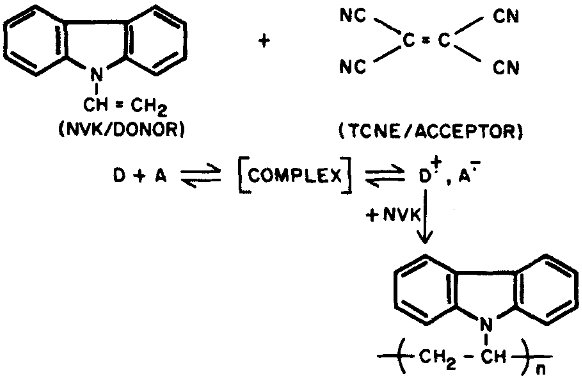


FIG. 17. Initiation of polymerization by charge-transfer complexes.

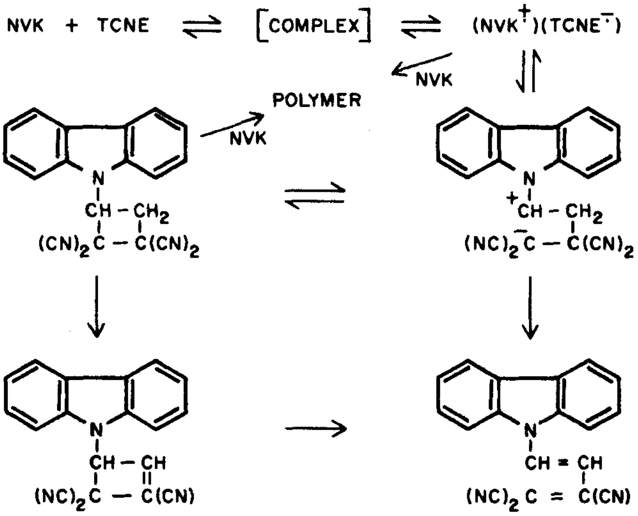


FIG. 18. Source of the reaction products found in the NVK/TCNE system.

issues arise from experimental methodology, i.e., system purity, role of solvent, effect of oxygen, etc., and this serves to re-emphasize the critical need to develop "clean" reaction systems. The extreme sensitivity of NVK to oxidation and the possible duality of polymerization

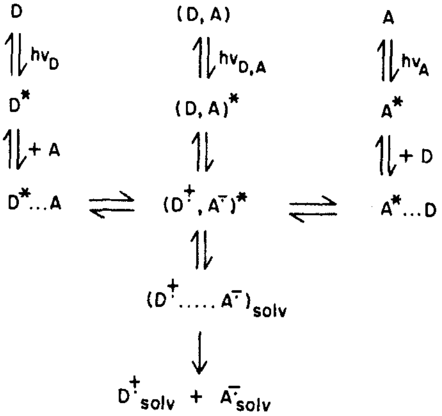


FIG. 19. Photoinduced ionic polymerization.

mechanism (radical and cationic) are particular disadvantages associated with this monomer, and a search for a superior model monomer would seem desirable.

Some very exciting work is appearing on the primary processes involved in photoionic polymerization. Ultrafast laser spectroscopic techniques are being used [23] to probe the nature and the reactions of the excited states involved in the initiation process. Early studies using α-methylstyrene will probably be extended to other monomer systems and will contribute significantly to our understanding of the fundamental processes involved in initiation of cationic polymerization.

CONCLUSIONS

I have touched on only a fraction of the topics in this broad field. A considerable effort is still required to place cationic polymerization on the same level of understanding as anionic. The goal of "living" carbenium ion polymers may yet be achieved. In a real sense it is the polymeric products of these vinyl aromatic polymerizations that are important. Can they leap the gap between laboratory curiosities and practical materials?

The range of monomers that can be polymerized ionically, the combinations that can be achieved, and the manner in which they can be combined (i.e., alternating, block, graft, stereocontrolled, etc.)

gives the technique almost unlimited potential. It is to be hoped that specialty applications will continue to develop [24]. In my opinion, the unique morphologies of many of these materials, and the materials properties that can be combined, have yet to be exploited. Their potential in the electronic, photochemical, medical, and other fields is great. It remains to be seen whether it will be realized.

ACKNOWLEDGMENT

I would like to thank my many colleagues at Xerox for their invaluable contributions to several of the research activities presented in this review and for their stimulating discussions on the ever-challenging topic of ionic polymerization.

REFERENCES

[1] A. Rembaum and A. Eisenberg, Macromol. Rev., 1, 57 (1966).
[2] M. Stolka, J. F. Yanus and J. M. Pearson, Presented at the North East Regional Meeting, American Chemical Society, Rochester, 1973; Submitted for Publication.
[3] J. M. Pearson, D. J. Williams, and M. Levy, J. Amer. Chem. Soc., 93, 5478 (1971).
[4] J. Jagur-Grodzinski and M. Szwarc, Ibid., 91, 7594 (1969).
[5] J. J. O'Malley, J. F. Yanus, and J. M. Pearson, Macromolecules, 5, 158 (1972).
[6] F. J. Burgess, A. V. Cunliffe, D. H. Richards, and P. Shadbolt, Eur. Polym. J., 10, 193 (1974).
[7] A. Rigo, M. Szwarc, and G. Sackmann, Macromolecules, 4, 622 (1971).
[8] A. Rembaum, A. M. Hermann, and R. Haack, J. Polym. Sci., B, 5, 407, (1967).
[9] W. W. Limburg, J. F. Yanus, A. Goedde, D. J. Williams, and J. M. Pearson, J. Polym. Sci., Polym. Chem. Ed., 13, 1133 (1975).
[10] P. Hyde, L. J. Kricka, A. Ledwith, and K. C. Smith, Polymer, 15, 387 (1974).
[11] K. Takemoto, J. Macromol. Sci.—Revs. Macromol. Chem., C5, 29 (1970).
[12] R. H. Michel, J. Polym. Sci., A2, 2533 (1964).
[13] B. E. Fleischfresser, W. J. Cheng, J. M. Pearson, and M. Szwarc, J. Amer. Chem. Soc., 90, 2172 (1968)

[14] G. Sauvet, J. P. Vairon, and P. Sigwalt, Bull. Soc. Chim. Fr., 1970, 4031.
[15] C. E. H. Bawn, F. A. Bell, and A. Ledwith, Chem. Commun., 1968, 599; D. C. Sherrington and A. Ledwith, Unpublished Results.
[16] P. M. Bowyer, A. Ledwith, and D. C. Sherrington, Polymer, 12, 509 (1971).
[17] L. P. Ellinger, Polymer, 6, 549 (1965).
[18] C. E. H. Bawn, A. Ledwith, and M. Sambhi, Ibid., 12, 209 (1971).
[19] T. Nakamura, M. Soma, T. Onishi, and K. Tamura, Makromol. Chem., 135, 341 (1970).
[20] S. Akoi, R. F. Tarvin, and J. K. Stille, Macromolecules, 3, 472 (1970); 5, 663 (1972).
[21] A. Ledwith, Acc. Chem. Res., 5, 133 (1972).
[22] K. Tada, Y. Shirota, and H. Mikawa, Macromolecules, 6, 9 (1973).
[23] M. Irie, H. Masuhara, K. Hayaski, and N. Mataga, J. Phys. Chem., 78, 341 (1974).
[24] J. M. Pearson, Polym. Preprints, 12, 68 (1971).