Macromolecules

Volume 12, Number 1 January–February 1979

Synthesis and Electronic Transport Properties of Polymers and Copolymers of β-*N*-Carbazolylethyl Vinyl Ether

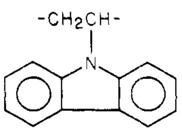
S. Richard Turner* and Damodar M. Pai

Joseph C. Wilson Center for Technology, Xerox Corporation, Rochester, New York 14644.

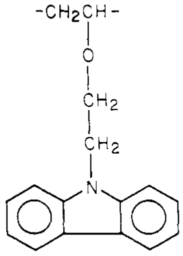
Received August 21, 1978

ABSTRACT: The monomer (β-*N*-carbazolylethyl vinyl ether) for these studies was prepared by direct condensation of β-chloroethyl vinyl ether with carbazole in KOH/Me_2SO. Homopolymerization was initiated with $BF_3{\cdot}OEt_2$ and $EtAlCl_2$. Alternating copolymers were readily prepared with maleic anhydride and N-substituted maleimides as comonomers. The electronic transport properties of poly(β-*N*-carbazolylethyl vinyl ether) and alternating copolymers of β-*N*-carbazolylethyl vinyl ether were measured by a xerographic discharge technique. Hole mobilities of the homopolymer were found to be similar to those reported for poly(*N*-vinylcarbazole). The alternating copolymers were also found to exhibit measurable hole mobilities.

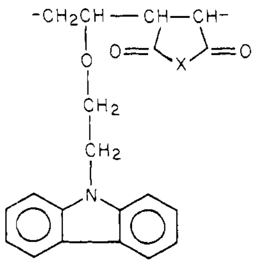
Interest in electronic transport in vinyl aromatic polymers is high from both theoretical and practical standpoints. The constraining influence of the polymer backbone on the pendant aromatic chromophores, leading to better overlap of these groups, is geneally believed to be an important factor in the electronic transport observed in such polymers. For example, poly(*N*–vinylcarbazole) (PVCz) (I) has been the subject of various structural studies[1] in order to establish if structural properties play a role in the photoconductive properties exhibited by PVCz.



I



II



III

X = O; X = N–R, where R = aromatic, $-CH_2OH$

In a recent publication[2] photoconductivity in poly(β-*N*-carbazolylethyl vinyl ether) (II) (PβCEVE) was compared to that in PVCz and based on the observation of lower steady state photocurrents in PβCEVE, the authors conclude that PβCEVE has a much lower hole mobility than PVCz. This lower mobility was interpreted in terms of a decreased electronic interaction between neighboring carbazole groups resulting from the larger distance between the pendant groups on the backbone. A model for photoconductive polymers was described that required that the transport moiety be placed close to the polymer backbone.

There is a problem with steady state photoconductivity measurements, however, in that they do not lend themselves to conclusions regarding mobility of the charge carriers especially in cases where the contacts are not ohmic. This situation is in fact expected to prevail when the polymer sample is sandwiched between NESA electrodes. Under these conditions the steady state photocurrent is equal to ηI, the product of the quantum efficiency of photogeneration η and the absorbed light intensity I in photons/cm^2 s. This is true even in the presence of carrier trapping since the traps do not show up in steady state with as many carriers trapping as are released from the traps. Therefore, barring any complications due to nonuniform electrical field within the film as a result of space charge buildup, the functional relationship between the photocurrent and the electric field should reflect the electric field dependence of η.

Recent disclosures[3,4] have shown that the photoconductive polymer model[2] with the transporting group

0024-9297/79/2212-0001$01.00/0 © 1979 American Chemical Society

connected directly to the polymer backbone is not a necessary condition for efficient electronic transport in organic systems. Molecular dispersions of *N*-isopropylcarbazole in bisphenol A polycarbonate, at much lower carbazole concentration than the carbazole concentration in PVCz, for example, exhibited hole mobilities comparable to PVCz at equivalent field strengths.[3] From this result it would appear that the position of the carbazole group (or other transport moiety) relative to the polymer backbone should not be important. Thus polymers like PβCEVE with the carbazole group extended from the backbone should be expected to yield good charge carrier mobilities.

This report describes our independent synthesis and electrical characterization of PβCEVE. We also report the first alternating copolymers (III) of βCEVE and their electronic properties. We have utilized a more direct measurement of charge carrier mobilities for these systems than the steady state photocurrent method used in ref 2.

Experimental Section

Monomer Synthesis. β-*N*-Carbazolylethyl Vinyl Ether. Powdered potassium hydroxide (34.0 g, 0.6 mol) was stirred in 200 mL of dimethyl sulfoxide under argon for 5–10 min. Carbazole (16.7 g, 0.1 mol) was added and the slurry stirred for 45 min. β-Chloroethyl vinyl ether (10.6 g, 0.1 mol) was added dropwise and the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was poured into 300 mL of water and the resulting white solid was recrystallyzed from ethanol to give 21 g (89%) of yellowish monomer. The crude product was chromatographed on silica gel with benzene/hexane (50/50). The still slightly yellow tinged monomer was recrystallized from 95% ethanol/activated charcoal and then hexane to yield 11.0 g (46.4%) of pure monomer, mp 80–81 °C (reported 79.0–80.5 °C. The NMR, IR, and elemental analysis were in agreement with the structure and agreed with the analytical data previously published.[2]

N-Substituted Maleimides. The N-substituted maleimides used in this study were prepared by known literature techniques[5] from their respective maleamic acids.

Polymerizations. Homopolymerization of β-*N*-Carbazolylethyl Vinyl Ether. a. $BF_3{\cdot}OEt_2$. In general, solvents for cationic polymerizations were purified by passing them through a neutral alumina column or by distillation from an appropriate drying agent. In a typical polymerization utilizing $BF_3{\cdot}OEt_2$ the monomer (1.0 g) was dissolved in 20 mL of toluene in a 100-mL three-necked round-bottomed blask equipped with a magnetic stirrer, a calcium chloride drying tube, a rubber septum for catalyst injection, and an inlet for argon. This apparatus was placed into an ice–water bath. The $BF_3{\cdot}OEt_2$ solution was also cooled to 0 °C before injection of ca. 1×10^{-5} mol. Immediately after addition a yellow color was noted. This was follwed by the solution becoming turbid and a white insoluble material separated. As the polymerization progressed, the color changed to a dark green with much white solid observed aroung the walls of the flask. After 3 h, the polymerization mixture was quenched in 300 mL of methanol in a blender. The off-white solid was completely redissolved in tetrahydrofuran and precipitated into hexane. A conversion of 0.8 g, 80%, of white solid was obtained. GPC analysis in tetrahydrofuran gave $\bar{A}_n$ = 188.7, $\bar{A}_w$ = 392.9, MWD = 2.08. This corresponded to $\bar{M}_n$ = 9400 determined by vapor pressure osmometry in tetrahydrofuran.

Anal. Calcd for $C_{16}H_{15}NO$: C, 81.00; H, 6.34; N, 5.90. Found: C, 81.06; H, 6.17; N, 5.91.

b. $EtAlCl_2$. Polymerizations with $EtAlCl_2$ as catalyst were conducted in methylene chloride at 0 °C. The monomer (1.0 g) was dissolved in 10 mL of the solvent and 4 wt % of the initiator was injected via a syringe. Immediately a dark green color developed. This slowly faded to blue green. After 5 h the reaction was quenched in 100 mL of methanol in a blender. Some material was left in the reaction vessel. A portion of this material dissolved in tetrahdrofuran and another portion was insoluble and apparently cross-linked. The soluble portion was precipitated into hexane. Both precipitants were combined, dissolved in tetrahydrofuran, and reprecipitated into hexane. After drying, 0.72 g (72% conversion) of white flocculant polymer was obtained. The GPC trace (THF) was binodal with the high molecular weight fraction yielding $\bar{A}_n$ = 550.6, $\bar{A}_w$ = 819.2 vs. $\bar{A}_n$ = 72.08, $\bar{A}_w$ = 195.8 for the low molecular weight fraction. This was equivalent to an $\bar{M}_n$ of 24 500 (high molcular weight fraction) using the *Q* value determined by VPO.

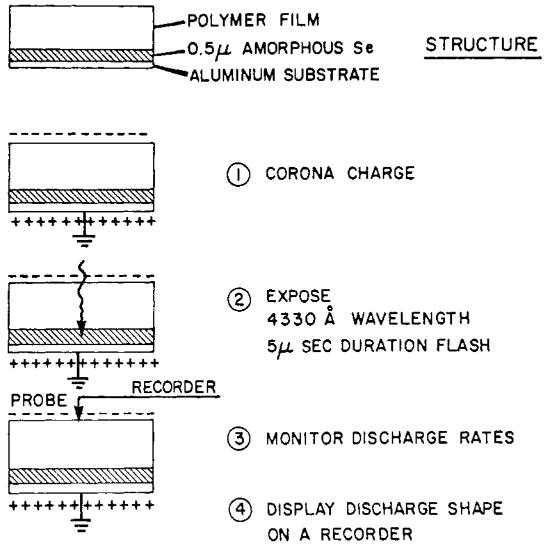


Figure 1. Schematics of the xerographic discharge technique used for obtaining charge carrier mobilities in transport polymer films.

Copolymerization of β-*N*-Carbazolylethyl Vinyl Ether. Copolymerizations were done in benzene solution using equimolar comonomer concentrations and AIBN as initiator. Polymer tubes were sealed under vacuum after two freeze–thaw cycles and the copolymerizations were carried out for 24 h at 60 °C. White powders were isolated and purified by reprecipitation techniques. Elemental analysis indicates a 1:1 composition for all polymerizable systems. The results are summarized in Table II.

Electrical Measurement Techniques

The charge transport measurements were performed using the xerographic discharge technique under space charge limited conditions. The layered device used for the study consisted of a polymer film solvent cast on a 0.5 μm thick amorphous Se layer which had been vapor deposited on an aluminum substrate maintained at 55 °C. The film was dried in a vacuum oven at 40 °C for several hours. The layered device is corona charged to a negative potential and is exposed to a light flash of 5 μs duration and 4330 Å wavelength. Since the polymer film is transparent at this wavelength, the incident light is absorbed in the a-Se, photogenerating holes which are subsequently injected into and drift across the polymer film. The surface charge of a device having a capacitance C ($=\epsilon\epsilon_0 A/L$) and charged to a potential V_0 is CV_0 in coulombs. The light flux in the flash source is adjusted to photogenerate more than CV_0 of free holes in the a-Se film. The ensuing discharge is monitored by a capacitively coupled probe and is time resolved. CV_0 is the maximum number of charges that can be injected into the film and the discharge under this condition is limited by the charge carrier mobility and is termed space charge limited (SCL) discharge. The transit time of the leading edge of the sheet of carriers is given by $T = V_0/2\ \mathrm{d}V/\mathrm{d}t$ where $\mathrm{d}V/\mathrm{d}t$ is the initial rate of discharge. The drift mobility (μ_d) is calculated from the relation $\mu_d = L^2/TV$ where L is the thickness of the polymer film. This measurement technique is schematically shown in Figure 1.

Results

βCEVE was synthesized by the direct coupling of β-chloroethyl vinyl ether and carbazole in potassium hy-

Table I
Summary of Homopolymerization Results for β-*N*-Carbazolylethyl Vinyl Ether

solvent[a]	initiator (concn mol)	temp, °C	time, h	conversion %	M_n[b]	M_w[b]
toluene	$BF_3 \cdot OEt_2$ (1×10^{-5})	0	2	70	3160	11200
methylene chloride	$BF_3 \cdot OEt_2$ (1×10^{-5})	0	2	80	2530	9550
nitroethane	$BF_3 \cdot OEt_2$ (1×10^{-5})	0	1	80	1760	4960
methylene chloride	tropylium (5×10^{-5}) tetrafluoroborate	0	1	30	very	low
methylene chloride	$EtAlCl_2$ (6×10^{-5})	0	4	70	21800 3050	29800 5700
methylene chloride	$EtAlCl_2$ (6×10^{-5})	−30	24	no pzn.[c]		
methylene chloride	$EtAlCl_2$ (6×10^{-5})	0	5	72	24500 3200	26450 8700

[a] Monomer concentration 10%. [b] Calculated from GPC results using the Q value determined by VPO. [c] Monomer not soluble at -30 °C.

Table II
Copolymerization Results for β-*N*-Carbazolylethyl Vinyl Ether with Maleimides and Maleic Anhydride

N substituent	% conversion	GPC parameters	
		A_n	A_w
2,4,6-trichlorophenyl	83	3795	11131
2,4-dichlorophenyl	84	1502	5407
4-chlorophenyl	32	993	2184
3-chlorophenyl	38	1077	2336
4-cyanophenyl	27	[a]	
4-nitrophenyl	no pzn.		
methylol	39	749	1943
2-anthraquinonyl	no pzn.		
maleic anhydride	80	620	1640

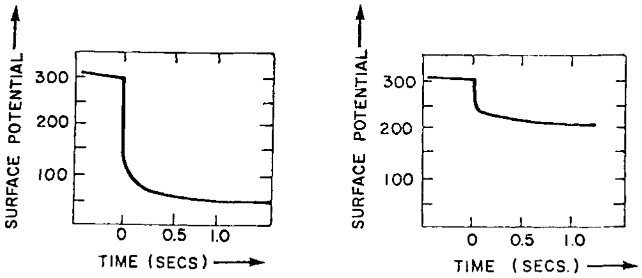
[a] Insoluble in tetrahydrofuran.

droxide/dimethyl sulfoxide. The monomer was easily purified and was found to readily homopolymerize with both $BF_3 \cdot OEt_2$ and $EtAlCl_2$. The homopolymerization results are summarized in Table I. $BF_3 \cdot OEt_2$ yielded rather low molecular weight polymer regardless of solvent. However, the molecular weights were significantly higher than those previously reported.[2]

Fragile thin films could be solvent cast from these materials. On the other hand $EtAlCl_2$ led to significantly higher molecular weight polymers, which were better film formers. At longer reaction times with $EtAlCl_2$, considerable insoluble material was formed presumably by cross-linking reactions. Only small amounts of insoluble material were observed in the $BF_3 \cdot OEt_2$ initiated polymerization. Polymerizations were not possible at temperatures lower than 0 °C because of monomer insolubility.

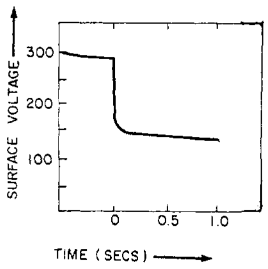
βCEVE was observed to readily copolymerize with electron acceptor monomers such as maleic anhydride and various N-substituted maleimides. The results are summarized in Table II. βCEVE was shown not to homopolymerize under the copolymerization conditions. All copolymers were found to be predominantly alternating. Color (CT complex) was observed on mixing the monomer solutions; however, no spontaneous copolymerization was observed. In the *N*-chlorinated phenyl cases the conversion and molecular weight appeared to be related to the withdrawing substituent on the *N*-phenyl (Table II). Higher molecular weights and faster relative rates of polymerization, as determined by conversion, were obtained as the electron acceptor strength increased.

Figure 2a shows a typical time resolved photoinduced discharge curve for PβCEVE. On the time scale of the display the initial rapid discharge is related to the leading edge of the carrier sheet at a higher mobility in the initial field E. As the discharge proceeds the trailing edge of the carrier sheet is in a lower field and therefore drifting with a lower mobility. The carrier velocity which is the product of the mobility and electric field is therefore considerably less for the trailing edge. This results in a considerable slowing down of the discharge rates as the potential across the device drops. The mobilities measured from the initial discharge rates of the SCL discharge are plotted as a function of electric field in Figure 3. For comparison purposes the mobility measured in a film of PVCz is shown in the figure. PVCz mobilities[4] have been reported to be between 10^{-6} and 10^{-7} cm^2/(V s) at 5×10^5 V/cm. In materials exhibiting a steep field dependence of mobility a small error in the measurement of the layer thickness can lead to a large error in the determination of the mobility. Nevertheless, the mobility measured in PβCEVE is very close to those reported for PVCz.



a. $BF_3 \cdot OEt_2$ initiated PβCEVE

b. $EtAlCl_2$ initiated PβCEVE



c. βCEVE-alt-N-(2,4,6-trichlorophenyl)maleimide

Figure 2. Time-resolved photoinduced discharge curves.

Figure 2b shows the time resolved xerographic discharge for a layered device of PβCEVE prepared from a different sample of polymer. The high residual potential results from a high level of bulk trapping in the film. We believe this trapping is associated with impurities in the film and is not an inherent property of the polymer since samples

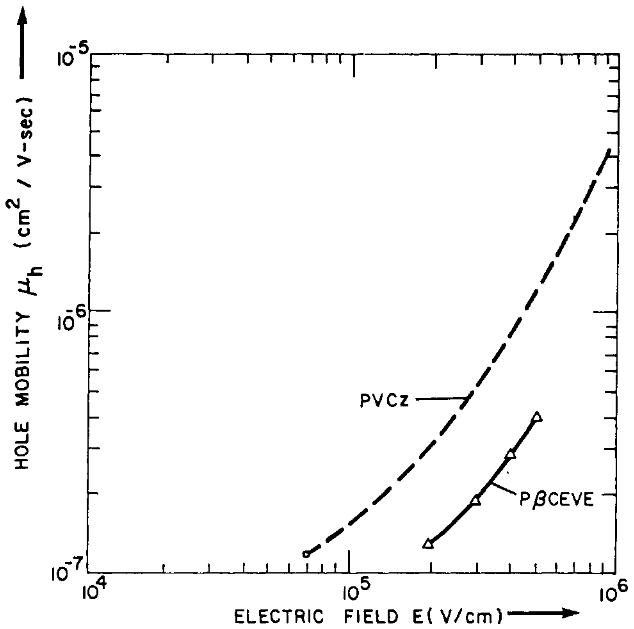


Figure 3. Hole mobility of PβCEVE and PVC as a function of electrical field.

with reduced trapping levels, as in Figure 2a, could be obtained. Although we do not know the nature of impurities that give rise to trapping, this result points to the critical role such impurities can play in this type of measurment.

All samples tested that were prepared by $EtAlCl_2$ initiation yielded this type of trap dominated discharge. This is thought to be due to impurity levels also. Elemental analysis indicated trace amounts of aluminum remained in the samples. X-ray diffraction measurements of both $BF_3{\cdot}OEt_2$ and $EtAlCl_2$ initiated polymers were identical and showed no order. NMR studies to determine tacticity of these polymers have not been done; however, the X-ray results are consistent with the difference in trapping levels being due to impurities rather than carbazole overlap differences resulting from regularity in the polymeric microstructure.

Figure 2c shows the time resolved discharge shape under SCL conditions for a layered device employing an alternating copolymer of βCEVE and *N*-(2,4,6-trichlorophenyl)maleimide. The thin nature of these films coupled with the high electric fields required to get a meaningful discharge made it difficult to time resolve the discharge curve. The rise time of the recorder sets a lower limit of transit time that can be resolved. Under the limitations of the experiment it is possible to predict only a lower limit for the mobility value and it is calculated to be larger than 5×10^{-8} cm^2 (V s) at a field of 7.5×10^5 V/cm. This charge carrier transport is clearly dominated by deep bulk trapping which is thought to be inherent to the sample since repeated purification by reprecipitation techniques did not change the level of the charge carrier trapping. Table III summarizes the electrical results for the copolymer. The copolymer from *N*-(4-chlorophenyl)maleimide was the only copolymer that did not exhibit measurable hole mobility.

Table III
Summary of Electrical Results for Copolymers of β-*N*-Carbazolylethyl Vinyl Ether

N substituent	μ_h^+, cm^2/(V s)	N substituent	μ_h^+, cm^2/(V s)
2,4,6-trichlorophenyl	$>5 \times 10^{-8}$ [a]	3-chlorophenyl	$>10^{-8}$ [a]
2,4-dichlorophenyl	$>10^{-8}$ [a]	methylol	$>10^{-8}$ [a]
4-chlorophenyl	$<10^{-8}$ [a]	maleic anhydride	$>10^{-8}$ [a]

[a] At 7.5×10^5 V/cm.

Conclusions

Our results clearly show that PβCEVE has a hole carrier mobility similar to PVCz at comparable field strengths even though the carbazole group is extended from the backbone. This result does not agree with the previous conclusions[2] regarding hole mobilities of PβCEVE. Our measurments of charge carrier mobility are more direct than the steady state technique used earlier and, thus, we believe they reflect the inherent electronic transport properties of PβCEVE.

We have also been able to measure hole mobilities in alternating copolymers of βCEVE and N-substituted maleimides. A lower limit of only about an order of magnitude less than PβCEVE at equivalent field strengths was observed despite the obvious interference to nearest neighbor carbazole chromophoric interactions. These are the first alternating carbazole-containing copolymers to exhibit measurable hole transport.

These results contradict the previously proposed model[2] for photoconductive polymers that required that the transporting group be directly attached to the polymer backbone as in PVCz. Attaching the photoactive group directly to the polymeric backbone for increased interactions is also not in agreement with the results of work on molecular dispersion of hole transporting active compounds in inert polymeric matrices.[3] For example, a 50% by weight dispersion of *N*-isopropylcarbazole in bisphenol A polycarbonate yields hole mobilities equivalent to PVCz where the carbazole concentration is much higher.[3] This result suggests that attaching the active pendant group directly to the backbone actually hinders electronic transport. Thus in conclusion we suggest that no simple steric model can be used for design of photoconductive polymers. Each system is probably controlled by its own morphological properties and thus generalizations in regard to backbone pendant group relationships may be misleading and probably have no importance.

References and Notes

(1) N. Tsuchihashi, M. Hatano, and J. Sohna, *Makromol. Chem.*, 177, 2739 (1976); W. W. Limburg and D. J. Williams, *Macromolecules*, 6, 787 (1973).
(2) K. Okamoto, A. Itaya, and S. Kusabayashi, *Polym. J.*, 7, 622 (1975).
(3) J. Mort, G. Pfister, and S. Grammatica, *Solid State Commun.*, 18, 693 (1976); G. Pfister, Abstracts of the American Chemical Society Meeting, Anaheim, March 1977.
(4) D. Pai, *J. Chem. Phys.*, 52, 2285 (1970).
(5) E. H. Huntress, K. Pfister, and K. H. T. Pfister, *J. Am. Chem. Soc.*, 64, 2845 (1942).