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Articles

Synthesis, Charge Transfer Complex Behavior, and Electronic Transport Properties of Novel Electron-Acceptor Polymers Based on Trinitrofluorenone

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ABSTRACT: Two novel aromatic electron-acceptor monomers based on the trinitrofluorenone nucleus have been synthesized and polymerized. These monomers, glycidyl 4,5,7-trinitro-9-fluorenone-2-carboxylate (I) and 2′-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate (II), were synthesized by coupling 4,5,7-trinitro-fluorenone-2-carboxoyl chloride with glycidol and 2-hydroxyethyl methacrylate, respectively. Polymerization was initiated by acidic ring-opening catalysts for I and by standard free-radical techniques for II. The electronic transport characteristics of the resulting low molecular weight polymers were investigated by a photodischarge technique. The charge transfer complex behavior of poly(2′-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate) was studied by utilizing *N*-isopropylcarbazole as donor.

Electron-acceptor polymers are of interest from a fundamental standpoint because of their potential to serve as electron transport molecules vis-à-vis the hole transport exhibited by electron-donor polymers like poly(*N*-vinylcarbazole). Specifically, the electron acceptor 2,4,7-trinitro-9-fluorenone (TNF) is known to possess excellent electron transport properties under an applied electric field in an amorphous film or in a polymeric matrix.[1] Therefore, polymers containing TNF would be of interest for their electron transport characteristics.

However, while the literature abounds with examples of electron-donor polymers, very few examples of electron-acceptor polymers have been reported. Most examples of electron-acceptor polymers have been prepared by step-growth techniques as exhibited in the reports of Schulz and Tanaka[2] and Sulzberg and Cotter.[3] Poly(2,4,7-trinitro-9-fluorenyl methacrylate), which we recently reported, is an example of an electron-acceptor polymer prepared by chain-growth techniques.[4]

The reasons for the lack of examples of electron-acceptor polymers are obvious. Conventional addition polymerization reactions become problematic in the presence of a strong electron acceptor. For example, for TNF-containing monomers, anionic polymerizations would fail because of electron-transfer reactions. Free-radical polymerization of most polymerizable groups would likewise not be promising because of electron transfer or other free-radical-inhibition processes by the nitro aromatic. Cationic techniques would appear feasible, but the monomer synthesis would require the incorporation of an electron-rich polymerizable group into a structure containing an electron poor acceptor—a potentially unstable situation.

This paper discusses the synthesis and polymerization of two TNF-containing monomers designed to circumvent the polymerization problems discussed above. The first monomer, glycidyl 4,5,7-trinitro-9-fluorenone-2-carboxylate (I), was designed to use ring-opening polymerization. The second monomer, 2′-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate (II) was chosen because the chain transfer of methacrylate to aromatic nitro compounds has been reported to be relatively small.[5] Our successful polymerization of 2,4,7-trinitro-9-fluorenyl methacrylate bears this point out.[4]

The electronic transport characteristics of these polymers and a model compound *n*-butyl 4,5,7-trinitro-9-fluorenone-2-carboxylate (III) were measured and compared to those reported for TNF. The charge transfer complex characteristics of these strong electron-acceptor polymers were also investigated.

Experimental Section

Monomer Synthesis. 4,5,7-Trinitrofluorenone-2-carboxylic Acid. This compound was synthesized by the method of Sulzberg and Cotter.[6]

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Table I
Polymerization of Glycidyl 4,5,7-Trinitrofluorenone-2-carboxylate

solvent	[monomer][a]	initiator	time, h	T, °C	% convrsn	M_n
methylene chloride	0.05	$BF_3 \cdot Et_2O$	2	0	46 (total)	
					29 (soluble)	1125
					17 (insoluble)	2070
toluene	0.12	diethylzinc/H_2O	24	room temp		
methylene chloride	0.17	diethylzinc/H_2O	18	room temp	75	b
tetrahydrofuran	0.17	diethylzinc/H_2O	18	room temp	3	b
toluene	0.10	triethylaluminum	3	room temp		c
methylene chloride	0.10	ethylaluminum dichloride	16	30	20	1440
	0.05		24	0	50	1980
	0.10		5	0	10	1215

[a] In g/mL. [b] Very low—possibly monomer. [c] Black solid; 8% Al present by elemental analysis.

4,5,7-Trinitrofluorenone-2-carboxoyl Chloride. The synthesis of this compound has been previously published.[7]

Glycidyl 4,5,7-Trinitro-9-fluorenone-2-carboxylate (I). 4,5,7-Trinitrofluorenone-2-carboxoyl chloride (10.0 g, 0.026 mol) was dissolved in 50 mL of tetrahydrofuran, and triethylamine (2.62 g, 0.026 mol) was added slowly. Glycidol (2.74 g, 0.037 mol), in excess, was dissolved in 10 mL of tetrahydrofuran and added dropwise. The mixture was allowed to stir for 30–45 min and then filtered. The amine salt residue was washed with 50 mL of tetrahydrofuran. The combined filtrates were flash evaporated and the black oily residue was taken up in 100 mL of chloroform. Any remaining salt was removed by extracting three times with 100 mL of water. The water layer was back-extracted with 100 mL of chloroform. The chloroform portions were combined and dried over magnesium sulfate. The chloroform was then flash evaporated until about 50 mL remained. At this point this solution was slowly added to about 800 mL of hexane and a light yellow powder resulted. The sample was redissolved and reprecipitated. After the precipitate was dried under vacuum, 7.9 g, a 73% yield, of product with a melting range of 65–75 °C was obtained. The NMR and IR spectra were fully consistent with the expected structure. As described in the text, further attempts at purification were all unsuccessful.

Anal. Calcd for $C_{17}H_9N_3O_{10}$: C, 49.10; H, 2.10; N, 10.10. Found: C, 49.39; H, 2.36; N, 10.49.

2′-Ethylmethacryl 4,5,7-Trinitro-9-fluorenone-2-carboxylate (II). This compound was prepared in a similar fashion to I, using 2-hydroxyethyl methacrylate in place of glycidol. Methylene chloride was used instead of chloroform in the workup. The product was a light yellow powder (81.5%) with a melting range of 60–70 °C. The NMR and IR spectra were consistent with the proposed structure.

Anal. Calcd for $C_{20}H_{13}O_{11}N_3$: C, 51.00; H, 2.76; N, 8.90. Found: C, 49.93; H, 2.70; N, 9.05.

***n*-Butyl 4,5,7-Trinitro-9-fluorenone-2-carboxylate (III).** The synthesis of this compound has been previously published.[7]

Polymerization. Polymerization of Glycidyl 4,5,7-Trinitro-9-fluorenone-2-carboxylate. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stirrer was charged with 1.0 g of the epoxide and 20 mL of methylene chloride (purified by passing down an alumina column). A deep brownish red solution formed. The initiator was boron trifluoride etherate, and it was prepared by diluting 1 mL of $BF_3 \cdot OEt_2$ to 10 mL with CH_2Cl_2. Both the reaction vessel and contents and the initiator were brought to 0 °C. A positive nitrogen pressure was kept on the reaction. The initiator (0.1 mL = 1 wt %) was introduced via a syringe through a rubber septum. Immediately a cloudiness appeared which was followed by a general lightening in the color of the solution. During the course of the 2-h polymerization time, solid deposited on the sides of the flask. The polymerization was quenched by pouring into methanol and the resulting solid weighed 0.29 g (A). The residue in the flask was dissolved in THF and precipitated into methanol (0.17 g) (B). The total conversion was 46%. GPC values for A were $\bar{A}_n = 11.0$, $\bar{A}_w = 25.0$, and MWD = 2.3 and for B were $\bar{A}_n = 20.0$, $\bar{A}_w = 46.3$, and MWD = 2.29. B corresponds to $\bar{M}_n$ of 2200, as determined by vapor pressure osmometry. The IR spectrum was consistent with the expected structure. The chemical analysis was in error as discussed in the text.

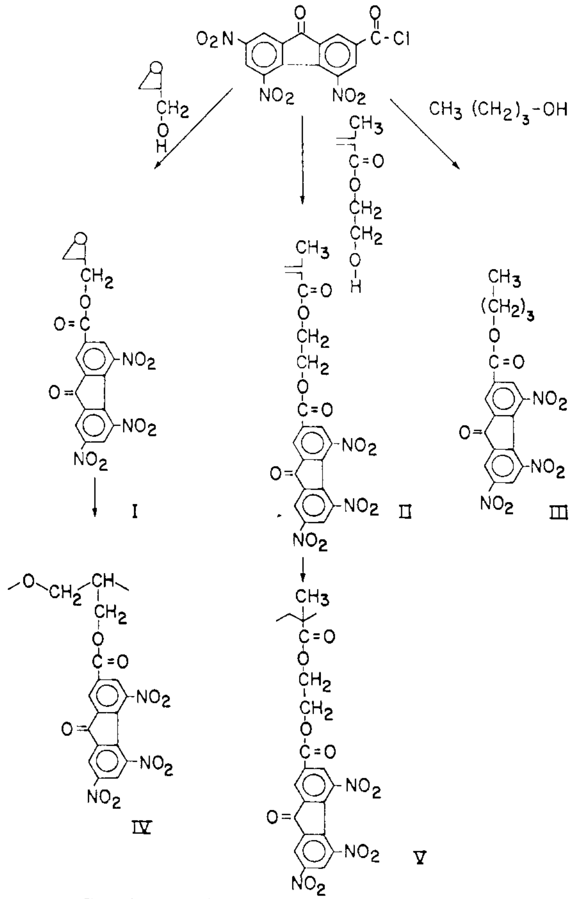

Figure 1. Synthetic scheme for trinitrofluorenone-containing monomers and model compound.

Polymerization of 2′-Ethylmethacryl 4,5,7-Trinitro-9-fluorenone-2-carboxylate. Into a polymer tube were added 2.5 g of the monomer, 8 mL of acetone (dried over 3A molecular sieves), and 0.025 g of AIBN (0.1 wt %). The tube and contents (red solution) were subjected to two freeze–thaw cycles before the tube was sealed under vacuum. The polymerization tube was then placed in a 60 °C bath and left for 17 h. No noticeable color or viscosity change occurred. Precipitation in methanol yielded 0.38 g of orange polymer (15%). GPC values were $\bar{A}_n = 88.9$, $\bar{A}_w = 116.7$, and MWD = 1.31. This corresponds to $\bar{M}_n$ of 3520 determined pressure osmometry (VPO). The IR spectrum was consistent with the proposed polymer structure (V). Films could be cast from acetone or tetrahydrofuran, although they proceeded to crack within a few days.

Anal. Calcd for $C_{20}H_{13}O_{11}N_3$: C, 51.00; H, 2.76; N, 8.90. Found: C, 51.88; H, 3.27; N, 8.98.

Electrical Measurements. The previously described xerographic discharge technique under space charge limited conditions was used for electrical characterization.[7-9] The layered device used for this study consisted of a polymer film cast on a 0.5-μm-thick amorphous Se layer.

UV Studies. Charge transfer complex studies and UV measurements were done on freshly prepared acceptor solutions in tetrahydrofuran as solvent.

Table II
Polymerization of 2′-Ethylmethacryl 4,5,7-Trinitrofluorenone-2-carboxylate

solvent	[monomer][a]	initiator	time, h	T, °C	% convrsn	M_n
acetone	0.31	1 wt % AIBN	17	60	15	3560
acetone	0.29	2 wt % AIBN	24	60	27	2550
acetone	0.50	2 wt % 2-MPP[b]	23	room temp	70[c]	very low
benzene	0.20	2 wt % AIBN	21	60	25	
chlorobenzene	0.50	2 wt % AIBN	17	60	36	very low
bulk		1 wt % AIBN	24	60		very low
emulsion (sodium oleate)		$K_2S_2O_8$		85		no polymn
emulsion (aersol OT)		$(NH_4)_2S_2O_8/NaHSO_3$		50		no polymn

[a] In g/mL. [b] 2-Methylpentanoyl peroxide. [c] Conversion is misleading since unreacted monomer was subsequently isolated from the product.

Results and Discussion

Monomer Synthesis. The acid chloride–alcohol condensation (Figure 1) reaction resulted in high yields of monomers I and II. However, both monomers were found to be extremely difficult to purify. The amorphous-like compounds were not recrystallizable from a variety of solvents and solvent mixtures. Chromatographic purification was likewise found to be unsuitable, as attempted purifications on alumina, silica gel, Florisil, and polyamide supports were all characterized by monomer absorption/chemical reaction problems. Reprecipitation techniques were utilized and the broad-melting powders that resulted gave NMR, IR, and elemental analysis data consistent with structures I and II.

Polymerization Studies. Glycidyl 4,5,7-trinitrofluorenone-2-carboxylate (I) was polymerized by several techniques that are normally used for epoxide ring-opening polymerizations. It appears that the strong, electronically active TNF moiety played a detrimental role in the polymerization process. As shown in Table I, boron trifluoride etherate was the most successful initiator for the polymerization. This initiator is known to lead to low molecular weight products in epoxide polymerizations because of the formation of cyclic oligomers etc.[10] This appeared to be the case for I since large quantities of initiator were necessary to obtain relatively low conversions. Molecular weights determined by VPO were around 2000. This is indicative of early termination reactions such as cyclizations. A complicating factor could be impurity effects since, as discussed earlier, the monomer was extremely difficult to purify.

The most successful catalysts found for oxirane ring-opening polymerizations have been the metal alkyls, e.g., diethylzinc and triethylaluminum. Several of these catalysts were tried and both diethylzinc and triethylaluminum were totally ineffective as polymerization initiators. It is believed that these catalysts, being somewhat basic in nature, complexed with the strong acceptor group and were thereby inactivated. Instantaneously, on addition, a dark color developed and precipitation occurred. For the triethylaluminum case, elemental analysis of the precipitate indicated a substantial amount of aluminum present, approximately 8%. In contrast, the more Lewis acid ethylaluminum dichloride system gave behavior similar to the boron trifluoride etherate initiation. Polymer was obtained, but large amounts of initiator were necessary. Even though UV and IR results were consistent with structure IV, the elemental analysis was in error.

2′-Ethylmethacryl 4,5,7-trinitrofluorenone-2-carboxylate (II) was subjected to several standard free-radical polymerization techniques (Table II). The best polymerization results were obtained when homogeneous solution techniques were used with azobis(isobutyronitrile) as the initiator. Conversion to about 30% and molecular weights of about 3500 (VPO) were obtainable. Attempts at emulsion polymerization failed, perhaps due to the inability to disperse the monomer sufficiently. A bulk polymerization was also unsuccessful.

Table III
UV Comparison of Polymers IV and V with Model Compound III[a]

compound	λ_{max}, nm	$10^{-3}\epsilon$
P(EMTNF) (V)	345	6.67
P(GTNF) (IV)	370	9.76
n-Bu-TNF (III)	350	6.89

[a] THF, room temperature.

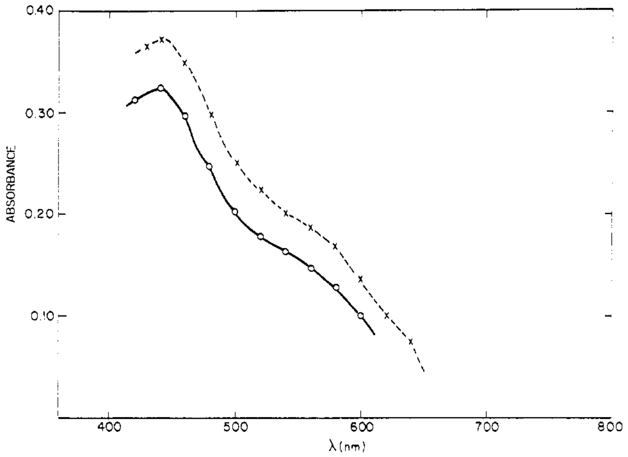

Figure 2. Charge-transfer absorbance of (○) *n*-Bu-TNF (III) and (×) P(EMTNF) (V) with *N*-isopropylcarbazole at 25 °C in THF. All concentrations 5 × 10^{-2} M.

It is felt that the difficulty in polymerizing this monomer to high molecular weight polymer results from the strong retarding effect of the trinitrofluorenone moiety. When compared to the free-radical polymerization of 2,4,7-trinitro-9-fluorenyl methacrylate,[4] the conversions and molecular weights are much lower under similar polymerization conditions. The electron affinity of the trinitrofluorenone ring is much higher than when the carbonyl group is reacted and the 9 carbon becomes sp^3 in character. Hence, it appears that the electron affinity of the acceptor is the important parameter for retardation of polymerization in these systems and not the number of nitro groups present. However, again, a qualifying statement that must be made is that, because of the problems encountered in monomer purification, some effect of impurity on molecular weight and conversion cannot be ruled out.

The UV spectra of polymers IV and V are very similar to the UV spectrum of the model compound III, as shown in Table III. This is taken as evidence corroborating the proposed polymer structures IV and V.

Charge Transfer Complex Studies. Polymeric donors have shown polymer chain effects on complex formation which are believed to be due to higher order complexes.[11] These effects have been characterized by the observation of values of λ_{max} for the polymeric systems being higher than those for the small-molecule analogues. Several examples have been documented, e.g., poly(*N*-ethyl-2-vinylphenothiazine) with trinitrofluorenone and poly(4-

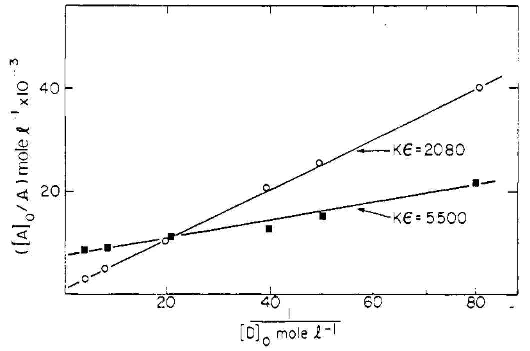

Figure 3. Benesi–Hildebrand plots for (■) P(EMTNF) (V) and (○) *n*-Bu-TNF (III) with *N*-isopropylcarbazole (440 nm, THF, 25 °C, 1-cm cell). $[A]_0$ = total acceptor concentration, $[D]_0$ = total donor concentration, and A = absorbance.

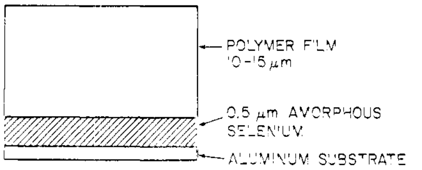

Figure 4. Layered device used for electrical testing of polymer films.

vinyl-4′-methoxybiphenyl) with chloranil; both exhibited substantially longer wavelength charge transfer complex λ_{max}'s than their corresponding model compounds complexed with the same acceptor.

In addition to shifts in λ_{max}, polymeric systems have been studied in comparison to their model systems for changes in the extent of charge-transfer complexation. This is usually determined by a Benesi–Hildebrand analysis where the product $K\epsilon$ is the most reliable parameter for comparison.

The charge-transfer behavior of polymer V and the model compound III were studied by utilizing *N*-isopropylcarbazole as the small-molecule donor. Little difference was observed in the λ_{max} in the charge-transfer bands of polymer V and the model compound III (Figure 2). Therefore, unique polymer chain effects that could result in polymer V being a better acceptor than compound III are apparently not present. Either the relative low molecular weight of polymer V or the fact that the acceptor group is spaced away from the polymer backbone could account for this effect. In our previous work on the charge-transfer behavior of poly(2,4,7-trinitro-9-fluorenyl methacrylate) with anthracene as donor,[4] a λ_{max} of 495 nm for the polymer was observed, contrasting with a value of 475 nm for the model system. This polymer possessed a significantly higher molecular weight and the acceptor chromophore was coupled closer to the polymer backbone.

The results of the Benesi–Hildebrand analysis for V and III with *N*-isopropylcarbazole are shown in Figure 3. In this analysis the polymeric system exhibited a somewhat higher extent of charge transfer complex formation than the model system. This result is consistent in magnitude with what has been observed in several donor polymer–small-molecule acceptor systems.[11]

Electronic Transport Properties. The electronic transport properties of polymers IV and V and the model compound III were studied by the previously described xerographic discharge techniques under space charge limited conditions.[7-9] The layered device used in these studies is shown in Figure 4 and consists of a solvent-cast polymer film on a 0.5-μm amorphous Se layer (any other well-characterized charge carrier generator can be used) that had been vapor deposited on an aluminum substrate. After the polymer surface was corona charged to a positive potential, the device was discharged with a 5000 Å light (to avoid light absorption in the transport polymer layer). In this experiment, under the space charge limited condition, one of the parameters controlling the discharge rate is the electron mobility in the polymer layer.

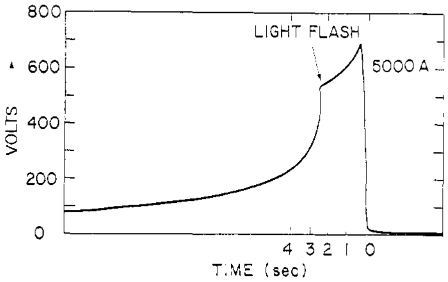

Figure 5. Typical photoinduced discharge curve obtained with P(EMTNF) (V). Film thickness ca. 8 μm.

The photoinduced discharge curve obtained by this technique for polymer V is shown in Figure 5. Using the known relationships between discharge rates, transit time, and drift mobility, an electron mobility of 2.8×10^{-8} $cm^2/(V\ s)$ at a field of 10^5 V/cm was determined for polymer V. This is the first reported example of electron transport in a synthetic polymer.

Unfortunately, this measurement for polymer IV was not possible because of the poor film-forming characteristics of this low molecular weight polymer. Attempts to make measurements with this polymer dissolved in a host-polymer binder led to discharge curves dominated by high levels of charge trapping and, therefore, it was not possible to obtain a value for the electron mobility in IV. This high level of trapping was most probably the result of either impurity levels in IV or morphological characteristics of the polymer blend.

An amorphous glass of the model compound III was studied by the same technique and a negative carrier mobility of 3×10^{-8} $cm^2/(V\ s)$ at a field of 10^5 V/cm was determined. This is in close agreement to that of polymer V.

The electron mobility of TNF, in an amorphous film has been determined to be 5×10^{-5} $cm^2/(V\ s)$ at 10^5 V/cm.[1] Comparison of the values of the electron mobilities of polymer V and model compound III to the TNF value reveals that these structures exhibit significantly lower electron mobilities than TNF. This result has been attributed for III to its higher electron affinity.[7] Because of the similar substitution pattern of polymer IV, similar reasons can be used to explain its lower electron mobility rather than invoking some type of polymer effect.

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