It is to be noted that c_{ij} and p_i are linear functions of cos ξ and sin ξ. Therefore, α, β, γ and α', β', γ' of eq 9 are linear and quadratic functions of cos ξ and sin ξ; α', β', γ' of eq 10 are polynomials of cos ξ and sin ξ of the third order. By solving eq 6 and 7 simultaneously, we have

$$\cos\eta = (\beta\gamma' - \gamma\beta')/(\alpha\beta' - \beta\alpha')$$
$$\sin\eta = (\gamma\alpha' - \alpha\gamma')/(\alpha\beta' - \beta\alpha') \qquad (11)$$

By squaring each of eq 11 and adding, we eliminate η and obtain an algebraic equation in a single unknown ξ.

$$(\beta\gamma' - \gamma\beta')^2 + (\gamma\alpha' - \alpha\gamma')^2 - (\alpha\beta' - \beta\alpha')^2 = 0 \qquad (12)$$

The left-hand side of this equation is a polynomial of cos ξ and sin ξ of the sixth (or, the 8th) order, when eq 9 (or, respectively, eq 10) is used for α', β', γ'. Real roots of this equation can easily be obtained numerically. If no helical structure with given values of unit height h and unit rotation ϕ is possible for the preassigned values of $\omega_1, \omega_2, \ldots, \omega_{m-2}$ and for any values of ω_{m-1} and ω_m (or ξ and η), then no real roots exist of eq 12. Once the value of ξ is determined by solving eq 12, the value of η can be determined by eq 11.

Special attention must be paid for the special cases of $\phi = 0$ and $\phi = \pi$. When $\phi = 0$, the polymer has the translational symmetry, and the matrix **U** becomes equal to the identity matrix **I**. This condition reduces the number of independent backbone dihedral angles by three. The additional condition that the unit height be equal to a given value h reduces the number by one more. In all, four backbone dihedral angles must be adjusted in order that a polymer has the translational symmetry with a given value of unit height h. This special case is excluded from the consideration in this paper of the general helical symmetries. When $\phi = \pi$, it is imperative to use eq 5 or 10 instead of eq 4 or 9. This is because the third term in the expression for γ' in eq 9 vanishes for $\phi = \pi$; thus, tailoring to the given height becomes impossible. We can avoid this difficulty by using eq 5 or 10.

References and Notes

(1) This work was supported by grants-in-aid from the Ministry of Education, Japan.

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Poly(2,4,7-trinitro-9-fluorenyl) Methacrylate. A New Electron Acceptor Polymer

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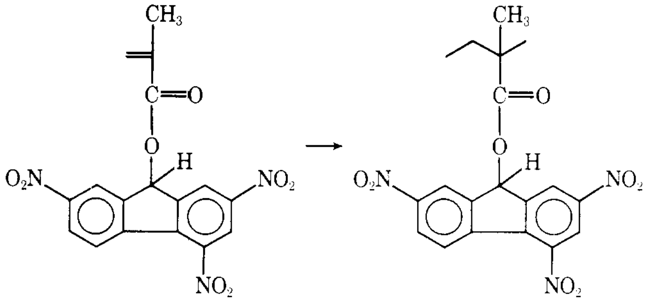
In contrast to the large number of electron donor type polymers that have been described in the literature, there have been very few reports of electron acceptor polymers. The ones that have been reported have, in the most part, dealt with the nitrated phenyl moiety[1-3] as the acceptor unit. Acceptor polymers based on polycyclic aromatic acceptors are rare indeed. A polyester based on the nitrated fluorenone nucleus has been reported by Sulzberg and Cotter[4] and Schulz and Tanaka[5] have reported polyesters based on the 9-spirocyclopropanetetranitrofluorene nucleus. This paper describes the preparation and some properties of an addition-type polycyclic aromatic acceptor polymer based on the trinitrofluorene nucleus poly(2,4,7-trinitro-9-fluorenyl) methacrylate (II).



I II (1)

Experimental Section

9-Diazo-2,4,7-trinitrofluorene (III). This compound was prepared according to the method by Colter and Wang[6] by first preparing 2,4,7-trinitrofluorenone hydrazone and then oxidizing to the diazo derivative with silver oxide in a yield of 75% (mp 214–215 °C) (lit.[6] mp 204–205 °C). The melting point was consistently higher than that reported over the course of several preparations.

2,4,7-Trinitro-9-fluorenyl Acetate (IV). This compound was prepared according to Colter and Wang[6] by refluxing 9-diazotrinitrofluorene in glacial acetic acid in a yield of 68% (mp 237–240 °C) (lit.[6] mp 240–242 °C).

2,4,7-Trinitro-9-fluorenyl Methacrylate (I). The diazotrinitrofluorene (10.0 g, 0.03 mol) was suspended in 150 ml of nitromethane and stirred with a magnetic stirrer. To this slurry 20 ml (0.22 mol) of freshly distilled methacrylic acid were added. Next, 4 ml of boron trifluoride etherate was added slowly via a syringe. Gas evolution was noted during addition. After stirring at room temperature for 1 h, a clear red solution resulted. The nitromethane was then removed on a rotary evaporator. When the pot material was reduced to an oil, the temperature was raised to 50 °C and the evaporation continued until an orange-yellow solid remained (approximately 1–2 h). Water (150 ml) was added to the flask and the contents were stirred at room temperature. After about an hour the suspension was filtered and then dissolved in 500 ml of benzene. This was heated to reflux and filtered hot to remove residual diazo compound. The benzene solution was evaporated on a rotary evaporator and the residual oil was allowed to solidify overnight. It was filtered, utilizing a minimum of ether, to effect the transfer. After drying at room temperature under vacuum for 24 h, 6.1 g (61%) of light orange powder (mp 148–150 °C) was obtained. The ir spectrum is shown in Figure 1a. NMR ($CDCl_3$) δ 2.0 (s, 3 H, CH_3), 5.65 and 6.15 (d, 2 H, $=CH_2$), 6.88 (s, 1 H, bridge H), 8.5 (m, 5 H, aromatic). Anal. Calcd for $C_{17}H_{12}N_3O_8$: C, 52.85; H, 3.11; N, 10.88. Found: C, 53.09; H, 2.91; N, 10.93.

Polymerization. A polymer tube was charged with 2.0 g of the monomer (I), 20 ml of reagent grade acetone, and 0.02 g (1 wt %) of AIBN. After three freeze–thaw cycles the tube was sealed under vacuum and placed into a 60 °C oil bath for 18 h. Precipitation into methanol yielded 1.5 g (75% conversion) of light yellow-orange powder which had an intrinsic viscosity at 30 °C in tetrahydrofuran of 0.128 dl g^{-1}. GPC analysis in tetrahydrofuran yielded $\bar{A}_n = 351$, $\bar{A}_w = 932$, MWD = 2.66. The ir spectrum is shown in Figure 1b. Anal. Calcd for $C_{17}H_{12}N_3O_8$: C, 52.85; H, 3.11; N, 10.88. Found: C, 52.85; H, 2.92; N, 11.07.

Uv Studies. Uv studies were done on a Cary Model 15 spectrophotometer utilizing fresh spectrograde tetrahydrofuran as solvent. All polymer solutions were run on the same day of preparation because of an apparent slow reaction of the solvent with the polymer leading to changes in the uv spectrum.

Results and Discussion

2,4,7-Trinitro-9-fluorenyl methacrylate (I) was prepared by the boron trifluoride etherate catalyzed reaction of 9-diazo-2,4,7-trinitrofluorene (III) with methacrylic acid in nitromethane (eq 2). Direct addition of methacrylic acid to III, as found by Colter and Wang[6] for acetic acid addition and described for the reaction of 9-anthryldiazomethane with acrylic acid,[7] was not possible since the methacrylic acid polymerized under the reaction conditions. Other attempts at preparing I through a solvolysis type reaction of 2,4,7-trinitro-9-fluorenyl tosylate and via the addition of methacryloyl chloride to 2,4,7-trinitro-9-fluorenol were all unsuccessful. The successful conditions, using a Lewis acid catalyst, were origi-

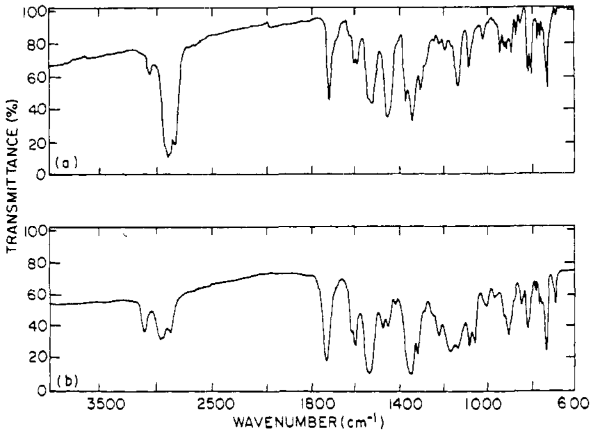
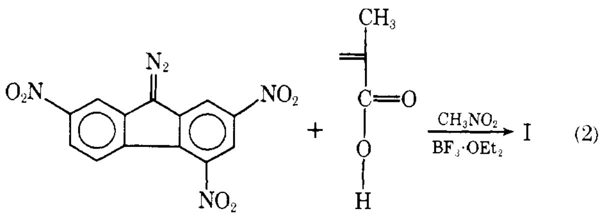
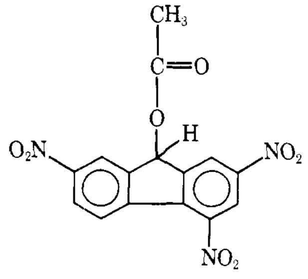


Figure 1. (a) Infrared spectrum (Nujol) of 2,4,7-trinitro-9-fluorenyl methacrylate. (b) Infrared spectrum (film) of poly(2,4,7-trinitro-9-fluorenyl) methacrylate.



III



IV

nally reported by Muller et al.[8] in the preparation of ethers from alcohols and diazoalkanes. Boron trifluoride etherate was the most successful of several Lewis acid catalysts that were tried in the preparation. Attempts to purify the monomer by recrystallization, chromatography, and precipitation techniques all led to material of lower melting point, hence the monomer utilized for polymerization studies was isolated, dried, and used directly without additional purification.

Polymerization. Because nitro aromatics are known free radical inhibitors, difficulty in polymerizing vinyl substituted nitro aromatics is expected and well documented (e.g., trinitrostyrene).[9] However, in contrast to the vinyl group, the chain transfer of methyl methacrylate to nitro aromatics in free radical polymerizations has been found to be relatively slow.[10] Indeed, some nitrophenyl methacrylates have been found to undergo free radical polymerization.[2] Thus, I was found, not unexpectedly, to polymerize readily by standard free radical techniques to relatively high molecular weight polymers. Brittle films were readily cast from tetrahydrofuran solution.

Table I gives the polymerization results and shows that acetone and tetrahydrofuran are the best solvents for the polymerization. Surprisingly, no polymerization occurred in benzene. In dimethylformamide and dimethyl sulfoxide the monomer formed a very dark solution, probably due to strong charge transfer interactions. The polymers isolated from these solvents were also highly colored, probably due to residual solvent.

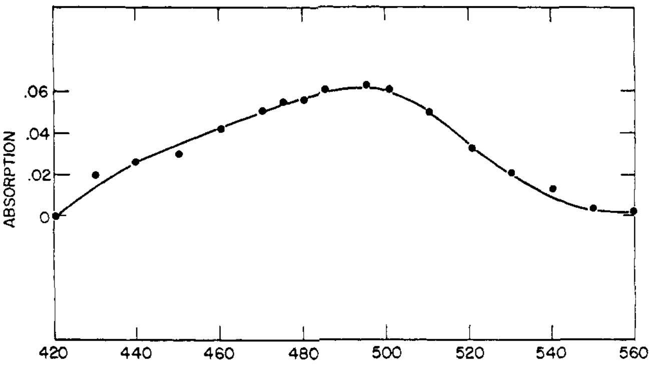


Figure 2. Charge transfer absorbance of poly(2,4,7-trinitro-9-fluorenyl) methacrylate/anthracene, 5 × 10^{-3} M, THF, 25 °C, 1-cm cell.

The resulting polymer was readily soluble in tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide. Since no major ir band changes were observed in going from monomer to polymer (Figures 1a and 1b) and since the uv spectrum of the polymer is very similar to the uv spectrum of the model compound 2,4,7-trinitro-9-fluorenyl acetate (IV) (as shown below in Table II), the structure of the polymer is thought to be the simple addition polymer (II). The λ_{max} have shifted to slightly longer wavelengths in the polymer.

Change Transfer Studies. This strong acceptor polymer readily complexes with donors as exemplified by its charge transfer complex with anthracene (Figure 2). The polymer complex has a λ_{max} at 495 nm vs. 475 nm in the corresponding small molecule model system, 2,4,7-trinitro-9-fluorenyl acetate (III) and anthracene. A Benesi–Hildebrand[11] analysis (Figure 3) of the polymer and anthracene in tetrahydrofuran gave a $K\epsilon$ of 2000 mol^{-2} l.^{2} cm^{-1} at 495 nm. The corresponding small molecule model system gave a $K\epsilon$ of 1100 mol^{-2} l.^{2} cm^{-1} at 475 nm. This compares favorably with previous results on a similar small molecule system, 2,4,7-trinitro-9-fluorenyl (+)-camphor-10-sulfonate and anthracene, which gave $K\epsilon$ = 1969 mol^{-2} l.^{2} cm^{-1} in acetic acid at 475 nm.[12]

Table I
Summary of Polymerization Studies of 2,4,7-Trinitro-9-fluorenyl Methacrylate

Solvent	Initiator Concn,[a] wt %	Time, h	% conversion
Benzene	0.1	24	
Acetonitrile	0.1	18	7
Dimethylformamide	0.1	24	10
Dimethyl sulfoxide	0.1	18	10
Acetone	0.1	18	10
Acetone	1.0	18	75
Tetrahydrofuran	1.0	24	66

[a] Azobisisobutyronitrile.

Table II
Uv Comparison of II and IV[a]

Compd	λ_{max}, nm	ϵ
Poly(2,4,7-trinitro-9-fluorenyl) methacrylate (II)	348	1.99×10^4
	320	1.70×10^4
2,4,7-Trinitro-9-fluorenyl acetate (IV)	340	1.88×10^4
	315	1.74×10^4

[a] Tetrahydrofuran solutions at room temperature.

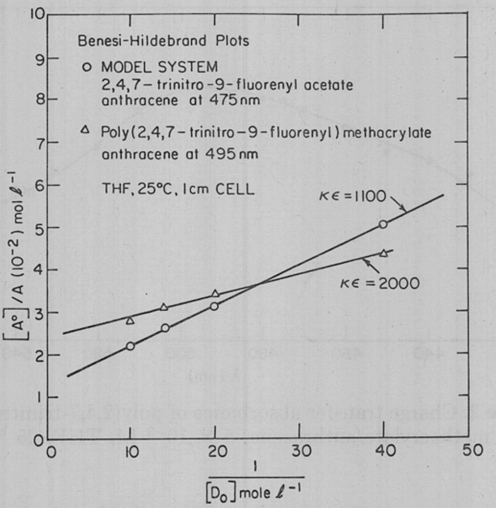


Figure 3. Benesi–Hildebrand plots for 2,4,7-trinitro-9-fluorenyl acetate/anthracene, 475 nm (○), and poly(2,4,7-trinitro-9-fluorenyl) methacrylate/anthracene, 495 nm (△); THF, 25 °C, 1-cm cell.

From these results the polymer charge transfer spectrum is shifted to longer wavelengths and in addition it appears that there may be some slight enhanced complexation in the polymeric acceptor when compared to the small molecule model. Examples of this type of behavior have been observed with polymeric systems before and have been somewhat nebulously described as "polymer effects".[13] Our results are qualified by several factors. The first is that the model acceptor IV is not exactly the repeat unit of the polymer and thus, the comparison may not be exact. A second factor is that the charge transfer bands of both the polymer and model systems have some asymmetry (Figure 2) indicating more complicated processes, other than simple 1:1 complexation, may be occurring. In addition, the accuracy of our uv studies is somewhat limited due to the poor solubility of anthracene, thus limiting the concentration range for the $K\epsilon$ determination. More studies are obviously necessary to fully characterize the complexing properties of this novel polymeric acceptor.

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Kink Bands in Modification II of Poly(vinylidene fluoride)

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Streaks along lines of constant ξ were found on the fiber diagram of modification II of poly(vinylidene fluoride), which could be obtained by annealing the oriented sample after attaching the ends to a metal holder. In this note, it is suggested that these streaks can be caused by the kink bands in the crystallite.

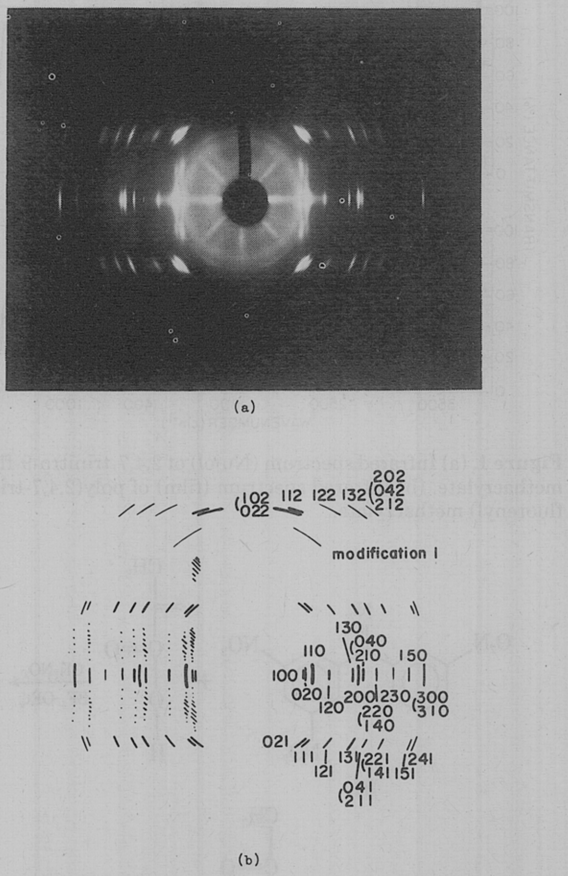

Figure 1. (a) Fiber photograph of modification II which gives the streaks and (b) its schematic representation.

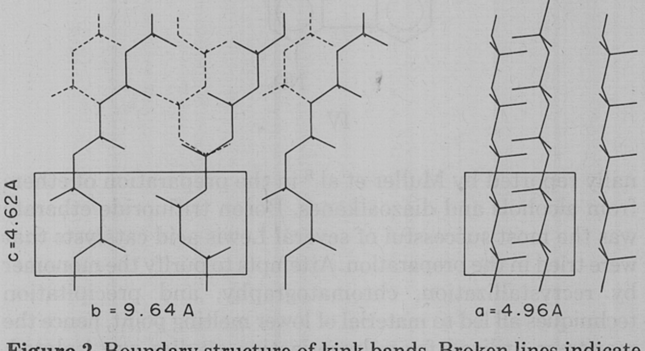

Figure 2. Boundary structure of kink bands. Broken lines indicate the structure of modification II. In the *b* projection, kink bands and modification II have the same structure.

A sample giving the streaks can usually be obtained by annealing an oriented sample of modification II at about 150 °C for about 24 h after fixing the ends on a metal holder. The oriented modification II was prepared by stretching a molten sample of KF-1100 (Kureha Chemical Industry Co., Ltd) at room temperature. Streaks have not yet been obtained from samples of Kynar 450 (Pennsalt Chemical Co., Ltd.).

As seen in the fiber photograph (Figure 1), the steaks have the following features: (1) they extend from Bragg reflections of modification II along lines of the constant ξ, (2) they are not observed in the $(h0\zeta)$, for example, (10ζ) and (20ζ), and the streak in the (02ζ) is the most intense, and (3) their intensity maxima are between layer lines of modification II. Feature (1) suggests that the disorder has the same periodicity as modi-