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Photoreactive Polymers. III. Photoisomerization of *cis*- and *trans*-Stilbene Sensitized by Poly(naphthoylstyrenes)

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ABSTRACT: Polystyrene was naphthoylated with α- and β-naphthoyl chloride. Physical measurements suggest that approximately two-thirds of the polystyrene phenyl rings were naphthoylated. The resultant polymers were used to sensitize the photoisomerization of *cis*- and *trans*-stilbene. They were found to have the same quantum efficiencies as did their corresponding model compounds except for the isomerization of *trans*-stilbene by the α-naphthoylated polymer. The uv absorbance and phosphorescence spectra of the polymers and model compounds were measured also.

Numerous examples can be found of intramolecular transfer of electronic excitation energy between two different chromophores connected by a variety of linkages,[1] and among many chromophores in polymers.[2] We were interested in studying how such polymers might differ as photochemical sensitizers from their monomeric counterparts. A polymeric sensitizer in which the excitation energy transfers intramolecularly up and down the chain of the polymer might be expected to be different from a monomeric sensitizer of the same chromophore in two important aspects. First, the rate of energy transfer to an acceptor might be greater[2c] because of its increased effective collisional radius.[3] Second, it might interact sterically with an acceptor during the energy transfer process and influence the mode of decay of the acceptor. The latter interaction could be pictured as a sort of cage effect in which the cage is the polymeric sensitizer molecule instead of several solvent molecules.

The photosiomerization of *cis*- and *trans*-stilbene was chosen as a probe for such effects. Fischer and his collaborators[4] demonstrated that there was a volume of activation for the trans–cis process so that it might be sensitive to steric interaction during the lifetime of the trans triplet. Also, it had been reported that the sum of the quantum yields for the trans → cis and cis → trans processes, ϕ_t and ϕ_c, respectively, was only 0.85 ± 0.01.[5] Thus, a 15% margin was apparently possible for increasing the quantum efficiencies. However, these numbers have recently been revised and the sum $\phi_t + \phi_c$ has been found to be unity, within experimental error.[6]

In part II of this series,[7] it was reported that ϕ_t and ϕ_c sensitized by poly(vinylbenzophenone) were the same as when sensitized by 4-methylbenzophenone. Moser and Cassidy[8] reported a similar result for poly(vinyl phenyl ketone). However, in extending this study to other polymers having similar chromophores we discovered one polymer, poly(α-naphthoylstyrene), for which ϕ_t was less than it was with the model compound. We report here the synthesis and some photochemical properties of polymers containing α- and β-naphthyl phenyl ketone chromophores, as well as several monomeric ketone models for the chromophores in them.

Experimental Section[9]

α-Naphthyl Phenyl Ketone. α-Naphthoyl chloride (25 g, 0.131 mol) was dissolved in 175 g of dry benzene under anhydrous conditions. To this solution was added 19 g (0.142 mol) of anhydrous aluminum chloride. This mixture was gradually warmed to reflux conditions and maintained under reflux for 1 hr. The reaction mixture was poured onto a mixture of concentrated hydrochloric acid and ice.

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[8] R. Moser and H. Cassidy, *Polym. Lett.*, **2**, 545 (1964).

[9] The Friedel–Crafts type of reactions described in the Experimental Section are modifications of methods referred to in C. P. Price, *Org. Reactions*, **3**, 16 (1946), and E. Miller and W. H. Hartung, *Org. Syn.*, **13**, 90 (1933).

The organic layer was separated, washed free of acid, and dried over anhydrous sodium sulfate. The dried solution was concentrated, giving an oily residue which was fractionally distilled. The main fraction of 116° (9 μ) was redistilled to 97° (5 μ) and then recrystallized twice from petroleum ether (bp 30–60°): mp 76° (lit.[10] mp 75.5–76°); yield 46.5%.

Anal. Calcd for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 88.2; H, 5.3.

β-Naphthyl Phenyl Ketone. This compound was prepared by the same procedure as the α isomer, mp 82° (lit.[11] mp 82°).

Anal. Calcd for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 87.8; H, 4.9.

Eastman 2-naphthyl phenyl ketone was also used.

2,4,6-Triethylphenyl α-Naphthyl Ketone. Anhydrous aluminum chloride (17.5 g, 0.13 mol) was added slowly to 50 ml of dry, freshly distilled ethylbenzene. To the suspension 25 g (0.136 mol) of α-naphthoyl chloride was added over a period of 30 min. The reaction mixture was warmed for 1 hr with stirring and then poured onto a mixture of hydrochloric acid and ice. The product was extracted with ether and the ether layer was washed free of acid with dilute sodium bicarbonate solution and dried over sodium sulfate. After the solvent was removed, the residual oil was distilled at 168° (3 μ). The crude product was recrystallized twice from ligroin, mp 108–110°. Gas chromatographic analysis on a 6 ft × $^{3}/_{16}$ in., 10% Apiezon column in an F & M 720 chromatograph at 290° revealed only one peak. The nmr and mass spectra were consistent with the structure assignment, 2,4,6-triethylphenyl 1-naphthyl ketone.

Anal. Calcd for $C_{23}H_{24}O$: C, 87.2; H, 7.6. Found: C, 86.8; H, 7.6.

2,4,6-Triethylphenyl β-Naphthyl Ketone. The same procedure that gave the α isomer was followed using β-naphthoyl chloride. A light-yellow oil was obtained, bp 117° (1 μ), n^{25}D 1.6225. From the oil, which showed several peaks on gas chromatographic analysis, was collected a major component using an Aerograph Autoprep fitted with a 20 ft × $^{3}/_{8}$ in., 10% SE-30–Chromosorb P column. This compound was shown to be 98–99% pure by gc analysis on an F & M 720 chromatograph fitted with a 6 ft × 0.25 in. 10% Apiezon column. The mass spectrum was consistent with that of triethylphenyl naphthyl ketone containing a small amount of diethyl derivative.

Anal. Calcd for $C_{23}H_{24}O$: C, 87.2; H, 7.6. Found: C, 87.4; H, 7.8.

***p*-Ethylphenyl α-Naphthyl Ketone.** Anhydrous aluminum chloride (19 g, 0.142 mol) was suspended in 100 ml of dry carbon disulfide. To this stirred suspension was slowly added 25 g (0.131 mol) of α-naphthoyl chloride. At reflux temperature, and with vigorous stirring, 10.6 g (0.11 mol) of dry ethylbenzene was added over a period of 30 min. After an additional 15 min of stirring under reflux the mixture was poured with vigorous stirring onto a mixture of ice and concentrated hydrochloric acid. The organic layer was separated and washed free of acid with water and dilute sodium carbonate solution. After drying over anhydrous potassium carbonate, the solvent was removed and the residual oil distilled to give four fractions. The fourth fraction, bp 128° (8 μ), was further purified by preparative gas chromatography on a chromatograph fitted with a 1 in. × 36 ft OV-17 column, followed by column chromatography using alumina and 5% ether in benzene solvent. Analytical glc analysis using an OV-17 column showed a purity of 99.7%; nmr, ir and mass spectra were consistent with the desired product.

TABLE I

ABSORBANCE DATA FOR POLY(NAPHTHOYLSTYRENES) AND THEIR MODELS[a]

Molecule	λ	a_λ, l./g cm	C.W. = (a_λ(model)/ a_λ(polymer)) MW(model)
Ia	310 nm	17.6	
	263 nm	51.6	
	6.05 μ	0.84	
NPK-1	308 nm	22.2	293
	250 nm	71.5	
	6.04 μ	1.12	310
EPNK-1	310 nm	17.3	246
	263 nm	53.2	
	6.04 μ	1.10	310
TEPNK-1	315 nm	26.4	475
	245 nm	66.3	
Ib	335 nm	8.7	
	287 nm	55.5	
	255 nm	104.0	
	6.05 μ	1.18	
NPK-2	335 nm	10.3	275
	285 nm	49.6	
	254 nm	136.0	
EPNK-2	332 nm	8.9	266
	284 nm	59.8	
	255 nm	121.0	
	6.05 μ	1.40	309
TEPNK-2	336 nm	6.7	244
	286 nm	39.8	
	255 nm	173	

[a] Spectra taken in chloroform solutions except for uv of NPK-2, which was taken in methanol solution. NPK = naphthyl phenyl ketone, EPNK = *p*-ethylphenyl naphthyl ketone, TEPNK = 2,4,6-triethylphenyl naphthyl ketone.

***p*-Ethylphenyl β-Naphthyl Ketone.** This compound was prepared in the manner used for the α isomer except that the reflux period after the addition of ethylbenzene was 1.5 hr. Distillation of the reaction product yielded four fractions. The final fraction, bp 123° (8 μ), still had the odor of acid chloride and was therefore refluxed 2 hr with aqueous sodium hydroxide. An ether extract of the reaction mixture was washed three times with water and dried over magnesium sulfate. Evaporation of the ether yielded a white solid, which, after recrystallization from *n*-hexane, melted at 77–81°. Ir and mass spectra were consistent with the assigned structure.

Poly(α-naphthoylstyrene). A solution of 10 g (0.096 mol) of polystyrene (Pressure Chemical Co.), special polystyrene, mol wt 4800, M_w/M_n <1:10, dissolved in 250 ml of dry carbon disulfide was treated with 15 g (0.112 mol) of anhydrous aluminum chloride and 16.6 g (0.0873 mol) of α-naphthoyl chloride under anhydrous conditions. The mixture was stirred at room temperature for 20 min, then heated under reflux 2 hr. The solvent was removed by distillation and the reaction solids were dissolved in dimethylformamide. The solution was slowly poured into four volumes of a mixture of ice and concentrated hydrochloric acid. The precipitated polymer was washed with methanol and reprecipitated twice from benzene into methanol.

Anal. Calcd for $C_{19}H_{14}O$: C, 88.4; H, 5.4. Found: C, 87.9; H, 5.6.

The molecular weight of the product was determined by membrane osmometry in dichloroethane at 35° to be 8900 ± 10%.

Poly(β-naphthoylstyrene). This polymer was prepared

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(10) M. Belti and P. Poccianti, *Gazz. Chim. Ital.*, **45**, 374 (1915).

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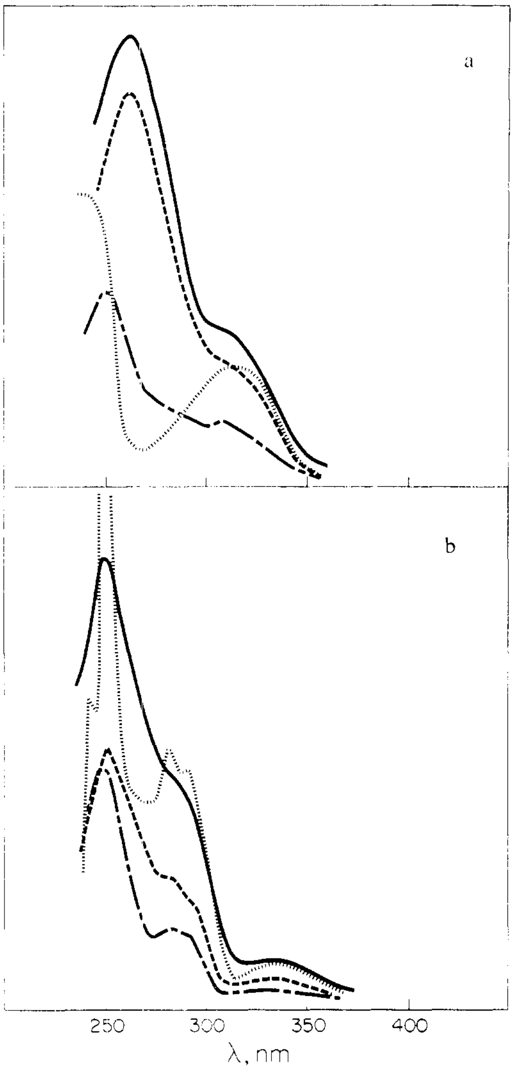


Figure 1. (a) Absorbance of poly (α-naphthoylstyrene) (—), 2,4,6-triethylphenyl naphthyl ketone (······), 4-ethylphenyl α-naphthyl ketone (– – –), and α-naphthyl phenyl ketone (-··-). (b) Absorbance of poly(β-naphthoylstyrene) (—), 4-ethylphenyl β-naphthyl ketone (– – –), β-naphthyl phenyl ketone (-··-), and 2,4,6-triethylphenyl β-naphthyl ketone (····).

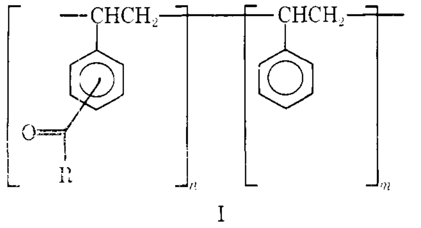
by the above procedure from the same batch of polystyrene as used for the α isomer.

Anal. Calcd for $C_{19}H_{14}O$: C, 88.4; H, 5.4. Found: C, 88.1; H, 5.6.

M_n was determined as above (8400 ± 10%). Procedures for purifying *cis*- and *trans*-stilbene and for measuring quantum yields and phosphorescence spectra were described earlier.[6,7]

Discussion

Poly(α-naphthoylstyrene) (Ia) and poly(β-naphthoylstyrene) (Ib) were prepared by naphthoylation of a polystyrene sample with a number average molecular weight of 4700 according to the method of Merrill and Unruh.[12] The model compounds α-naphthyl 4-ethylphenyl, and β-naphthyl 4-ethylphenyl ketones were synthesized by a modified Friedel–Crafts reaction. Without the modification, an intermolecular trans-alkylation reaction occurs, leading to 2,4,6-triethylphenyl naphthyl ketones in the case where ethylbenzene is naphthoylated. The uv data of the product polymers and model compounds are reported in Table I and Figure 1. Inspection of Figure 1 reveals that the *p*-ethylphenyl naphthyl ketones are the best of the models for the chromophores in the polymers. The α-naphthyl series in particular is sensitive to the degree of alkylation in the benzoyl group. The absorbance, in units of liters per gram, was used to calculate the "chromophore weight" (C.W.) in the polymer by equating the extinction coefficient of the chromophore in the polymer with the extinction coefficient in the model. The C.W.'s thus calculated using the uv long-wavelength



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Ia, R = α-napthyl
b, R = β-naphthyl

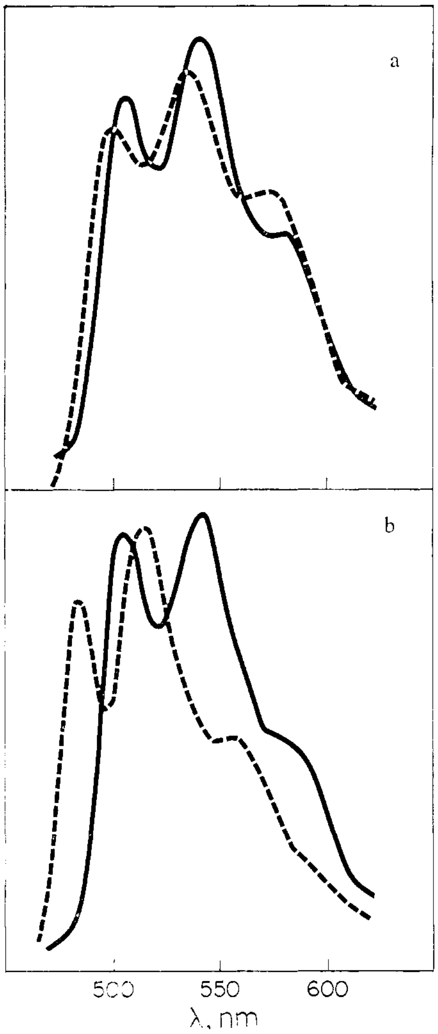

Figure 2. (a) Phosphorescence (77 °K) of poly(α-naphthoylstyrene) (—) and *p*-ethylphenyl α-naphthyl ketone (– – –) in 2-methyltetrahydrofuran. (b) Phosphorescence (77 °K) of poly(β-naphthoylstyrene) (—) and *p*-ethylphenyl β-naphthoyl ketone (– – –) in 2-methyltetrahydrofuran.

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[12] S. H. Merrill and C. C. Unruh, U.S. Patent 2,831,768 (April 22, 1958).

TABLE II
PHOSPHORESCENCE DATA FOR POLY(NAPHTHOYLSTYRENES) AND THEIR MODELS

		Energy, kcal[c]							
		Edge		0–0		0–1		0–2	
Sensitizer[a]	τ, msec[b]	Glass	Film	Glass	Film	Glass	Film	Glass	Film
PVBP	1.0	71.9	69.2	68.3	65.7	63.8	61.5	59.3	57.2
BP	2.2[d]	11.5	68.6	68.0	66.2	62.9	61.6	60.2	
MBP		72.6	69.2	68.6	65.7	64.3	61.5	60.0	57.2
Ia	190	59.3	56.0	56.3	52.9	52.8	49.1	49.0	45.6
NPK-1		59.5		56.3		53.2		49.3	
EPNK-1	570	60.1		57.4		53.6		50.0	
TEPNK-1	137	58.0	55.5	55.4	52.7	51.6	49.0		45.6
Ib	202	59.6	56.3	56.3	53.8	52.6	49.7	49.3	45.6
NPK-2		60.6		58.4		54.4		50.8	
EPNK-2	490	61.0	57.0	58.3	54.5	54.5	49.6		
TEPNK-2		60.7	57.1	57.9	54.8	54.3	50.7		

[a] PVBP = poly(vinylbenzophenone), BP = benzophenone, MBP = 4-methylbenzophenone, NPK = naphthyl phenyl ketone, EPNK = *p*-ethylphenyl naphthyl ketone, TEPNK = 2,4,6-triethylphenyl naphthyl ketone. [b] Undegassed, unannealed, 10^{-4} *M* 2-methyltetrahydrofuran glasses. [c] Glasses for polymers were made from freshly distilled 4-methyltetrahydrofuran without degassing or annealing, those for monomers were similarly made from EPA. Films were cast from a chloroform solution. Two parts polystyrene was used to obtain films for monomers. Maximum error in reading energies from spectra is estimated to be ±0.3 kcal. [d] At 10^{-5} *M* a degassed sample had a lifetime of 5.8 msec and an undegassed sample had a lifetime of 1.2 msec.

TABLE III
QUANTUM YIELDS FOR ISOMERIZATION OF *cis*- AND *trans*-STILBENE

Sensitizer[a]	Stilbene, *M*	ϕ_c	ϕ_t
PVBP	0.06		0.55[b]
	0.05	0.46[c]	0.54, 0.59
BP	0.2		0.56[c]
MBP	0.05		0.56[c]
	0.09	0.42[d]	
Ia	0.04	0.42, 0.44, 0.43, 0.44	
	0.05		0.46, 0.44, 0.43, 0.45
	0.06		0.45
Ia-900[e]	0.05		0.51,[f] 0.49,[f] 0.49[f]
EPNK-1	0.05		0.56[c]
TEPNK-1	0.04	0.41[d]	0.57[d]
	0.05		0.56[d]
	0.06		0.54
Ib	0.04	0.43, 0.44	
	0.05	0.41	0.58, 0.56, 0.55
	0.06		0.51, 0.53
NPK-2	0.05		0.56[c]
EPNK-2	0.05		0.53[c]
TEPNK-2	0.05	0.43[d]	0.57[c]

[a] PVBP = poly(vinylbenzophenone), BP = benzophenone, MBP = 4-methylbenzophenone, EPNK = *p*-ethylphenyl naphthyl ketone, TEPNK = 2,4,6-triethylphenyl naphthyl ketone, NPK = naphthyl phenyl ketone. [b] Relative to MBP, assuming ϕ_t = 0.56 for MBP. [c] Reference 7. [d] Reference 6. [e] From naphthoylation of 900 mol wt polystyrene. [f] Relative to Ib, assuming ϕ_t = 0.55 for Ib.

absorbance and the *p*-ethylphenyl models were 246 for Ia and 266 for Ib. The 605-μ ir band indicated that C.W. is ~310 for both polymers. When these values of C.W. are used to calculate the number of naphthoyl units per styrene unit, the results are 1.1 and 0.9 for the uv method and 0.67 for the ir method. Calculation of these numbers from a comparison of direct measurements of the number average molecular weight of the polymer and the number average molecular weight of the starting polystyrene gives 0.53 for Ia and 0.60 for Ib. Mass spectra of pyrolyzed samples of the polymers show no evidence for there being more than one naphthoyl group on a single styrene unit.

The phosphorescence spectra of the sensitizers are shown in Figure 2 and are summarized in Table II, which gives the energies of important features. The spectra were recorded at 77°K from undegassed, unannealed organic glasses and polymer films. The polymer film spectra of the monomeric sensitizers were obtained from coatings of the sensitizer in polystyrene. In general, the phosphorescence spectra contained three distinguishable bands, the middle band usually being the most intense. The difference in phosphorescent energies between the polymeric chromophores and their monomeric models are small and appear to depend on the degree of substitution about the phenyl ring as well as on the nature of the second aryl group. Thus, the 0–0 band of the poly(vinylbenzophenone) phosphorescence spectrum taken in an organic glass is shifted −0.3 kcal relative to the *p*-alkyl model, whereas this shift is −0.7 kcal for Ia and −2.0 kcal for Ib. These shifts were reduced to 0.0 for poly(vinylbenzophenone) and −0.7 for Ib when the spectra were recorded from their films, where all of the spectra are about 1–2 kcal lower than in organic glasses.

Quantum yields for the sensitized photoisomerization of *cis*- and *trans*-stilbene were measured in degassed benzene solutions using light of 366-nm wavelength. The results for the monomeric models have been reported elsewhere.[6] The results for the polymeric sensitizers are reported in Table III along with a summary of the monomer values. These results show that the polymers poly(vinylbenzophenone) and poly(β-naphthoylstyrene) sensitize the isomerization of stilbene with the same efficiency as do the corresponding models. However, poly(α-naphthoylstyrene) is less efficient than are its corresponding models in the case of the trans → cis process. Furthermore, the inefficiency for the α-naphthoyl polymer is related to the chain length of the polymer. Thus, when polystyrene of molecular weight 4700 was treated with α-naphthoyl chloride, the resultant polymer had a ϕ_t of 0.45 ± 0.01 while the polymer prepared by naphthoylation of a polystyrene with molecular weight 900 had ϕ_t of 0.49 ± 0.01.

The inefficiency of the α-naphthoylated polymers in sensitizing the trans → cis isomerization of stilbene could be explained on the basis of the steric requirements of the α-naphthoyl group. Such steric requirements could force the polymer into a configuration which would bury the internal chromophores and make them inaccessible to acceptor molecules. However, ϕ_c is normal for poly(α-naphthoylstyrene) and this implies that all of the excitation energy in this polymer is available for sensitization. Thus, it appears that the inefficiency in ϕ_t must be due to an induced inefficiency in the use of the excitation energy by the sensitized molecule of *trans*-stilbene. We believe this is the result of the positive volume of activation noted by Fischer[4] for the trans → cis process. Accordingly we envision the excited *trans*-stilbene molecules to be confined for a time in a polymeric cage which restricts their rotation. Thus, some of the excited stilbene molecules would decay to the ground state before proceeding to the twisted triplet, which is responsible for isomerization.[4] The fact that ϕ_c is not lower for poly(α-naphthoylstyrene) may be explained by the lack of a volume of activation for the cis → trans process.[4] It is believed that this explanation is more than just a local visocisty effect since the β-naphthoyl polymer would also be expected to show such an effect.

Aminimides. VIII.[1a] Synthesis and Homo- and Copolymerization Studies of 1,1,1-Trimethylacrylylhydrazinium Chloride and 1,1,1-Trimethylmethacrylylhydrazinium Chloride[1b]

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ABSTRACT: The monomers 1,1,1-trimethylacrylylhydrazinium chloride (II) and 1,1,1-trimethylmethacrylylhydrazinium chloride (III) were synthesized and shown to readily homo- and copolymerize with a variety of other vinyl monomers to produce copolymers containing pendent quaternary residues ($-CONHNR_3^+X^-$). The resultant polymers were treated with base to provide "reactive polymers" with pendent aminimide groups ($CON^-N^+R_3$). Since molecules with aminimide residues suffer a carbon–nitrogen migration reaction on heating, the aforesaid aminimide polymers were thermolyzed both in solution and the solid phase to provide unique, "reactive polymers" with pendent secondary or tertiary isocyanate groups. The reactivity ratios of each monomer (M_1) with styrene (M_2) were determined: monomer II, $r_1 = 0.46$, $r_2 = 0.58$; monomer III, $r_1 = 0.23$, $r_2 = 0.51$. The Alfrey–Price Q and e values were also calculated: $Q = 0.69$, $e = 0.34$ and $Q = 0.61$, $e = 0.66$, respectively.

Studies in several laboratories have shown that both aliphatic and aromatic compounds with ammonium acylimine residues of the type $-CON^-N^+R_3$ suffer a carbon–nitrogen migration reaction during pyrolysis,[2–4] yielding tertiary amines and isocyanates. In a prior publication,[1b] we described the preparation and polymerization properties of trimethylammonium-*N*-methacryloylimine (I, trimethylamine methacrylimide). The cited work demonstrated that monomers such as I

$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CON^{-}N^{+}(CH_3)_3}$$

I

are highly useful for preparing a wide variety of reactive polymers.

The present work was undertaken to prepare and to study some of the homo- and copolymerization characteristics of 1,1,1-trimethylacrylylhydrazinium chloride

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(1) (a) Presented in part to the Polymer Division at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 5, 1970; (b) for paper IV in this series, see B. M. Culbertson and R. C. Slagel, *J. Polym. Sci., Part A-1*, **6**, 363 (1968).

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