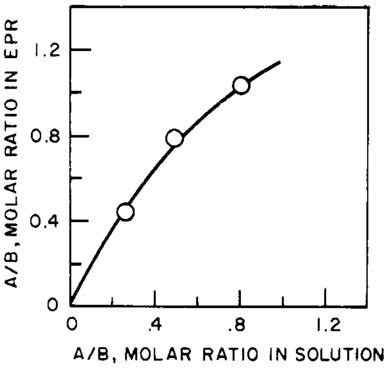

Figure 4. Equilibrium ratio of acrylic acid monomer to C_7 ester monomer which actually is contained in epr *vs.* ratio of acrylic acid monomer to C_7 ester monomer in the swelling solution.

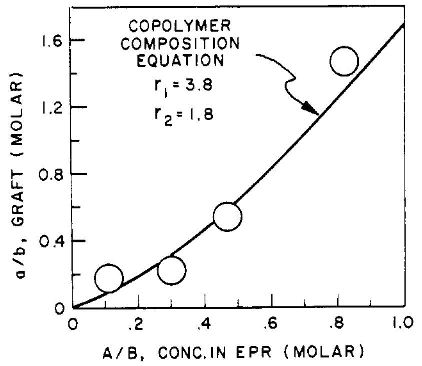

Figure 5. Ratio of acrylic acid to C_7 ester in graft copolymer *vs.* ratio of acrylic acid monomer to C_7 ester monomer actually contained in the epr.

Conclusions

Our results indicate that, aside from the polar influences or steric effects described by Odian and coworkers,[8] the composition of a graft formed from a substrate swollen by a comonomer solution may be predicted by the two-component copolymer composition equation.

Acknowledgment. The authors take pleasure in acknowledging Mr. John Parsons for his valuable assistance in the use and calibrations of the attenuated total reflectance infrared system used for this study.

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(8) G. C. Odian, A. Rossi, and E. N. Trachtenberg, *J. Polym. Sci.*, 42, 140 (1960).

The Role of Hydrogen Bonding in the Photochemistry of Poly(*t*-butyl N-vinylcarbamate)

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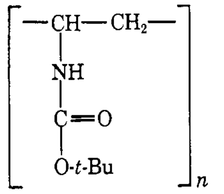
ABSTRACT: The quantum yield (ϕ_{II}) for cycloelimination of isobutene and CO_2 from thin films of poly(*t*-butyl N-vinylcarbamate) was found to be 0.01. In contrast, quantum yields in alcoholic solvents were 0.04 and hydrocarbon media gave values of 0.16. From the solvent shifts of the electronic spectra and approximate phosphorescence lifetimes, the lowest reactive excited state of the polymer in hydrocarbon solvents was deduced to be of $n-\pi^*$ character while in alcoholic solvents and film form a carbonyl $\pi-\pi^*$ excited state abstracted the β-ester proton. It was found that intermolecular hydrogen bonding ($N-H\cdots O=C$) of the *gauche* rotamer of the ester moiety played a significant role in reducing the quantum yield in thin films. Evidence for this was gained from solution and thin film infrared spectra data analyzed relative to the temperature dependence of the cycloelimination quantum yield.

Previous studies[1] on the solid-state photochemistry of poly(*t*-butyl acrylate) have shown that the primary process is a Norrish type II elimination yielding isobutene and poly(acrylic acid). In addition, the photoreaction was found to take place from an $n-\pi^*$ state of the carbonyl group.[1b] Another aspect of the previous work was that a photoinduced rotational isomerization occurred between the *cis* and *gauche* forms of the ester with subsequent cycloelimination from the *cis* rotamer. The present study pertains to a relationship between the photochemical and spectroscopic properties of poly(*t*-butyl N-vinylcarbamate). Com-



$$\left[-\underset{\substack{| \\ NH \\ | \\ C=O \\ | \\ O\text{-}t\text{-}Bu}}{CH}-CH_2- \right]_n$$

parative experiments were made with poly(*t*-butyl acrylate) to understand better the effect of the amino group between the polymer backbone and ester group. Particular emphasis was given to details of the nature of the excited states involved and intermolecular bonding of the carbamate (CO–NH) group to rationalize differences between the polycarbamate and polyacrylate

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(1) (a) A. R. Monahan, *J. Polym. Sci., Part A-1*, 4, 2381 (1966); (b) *ibid.*, 5, 2333 (1967).

solid phase quantum yields (ϕ_{II}). Variations in ϕ_{II} for the polycarbamate in film form and in alcoholic and hydrocarbon solvents were examined in relation to inversion of excited states and intermolecular hydrogen bonding.

Recent work on similar photoprocesses in substituted aromatic ketones and esters has established that the electron density distribution about the carbonyl group has a profound effect on its inter-[2a] or intramolecular[2b] hydrogen atom abstracting ability. Such results have been explained in terms of the relative transition energies and reactivities of n–π^* and π–π^* states. The n–π^* type of excitation results in a reduction in charge on the oxygen atom, whereas the π–π^* state yields an increased negative charge on the carbonyl. The relative position of states in a molecule could be altered by changing the electron-donating character of the substituent or solvent polarity.[3] The gradations in triplet lifetimes of 4-aminobenzophenone with variation in solvent polarity[3] indicated that an inversion in levels did not necessarily yield states with completely separate identities but rather a mixing of levels can occur.

To date, no detailed photochemical study of any carbamate has been reported. The work of Booth and Norrish[4] on monomeric amides gave further impetus to our work because type II eliminations were found in a variety of amide compounds containing γ-alkyl hydrogens.

Finally, since carbamates are monourethanes, the photochemical study of this system may gain insights into efficient ways of stabilizing polyurethanes.

Experimental Section

A. **Materials.** The sample of poly(*t*-butyl N-vinylcarbamate) (I) was supplied by Dr. H. James Harwood of the University of Akron. The synthesis, elemental analysis and thermal decomposition have been reported by Harwood.[5] The molecular weight of I was found to be 160,000, using a Hewlitt-Packard No. 502 high-speed membrane osmometer. A Du Pont differential thermal analyzer gave a value of 120° for the glass transition temperature and a melting point of 263°. The model compound, *t*-butyl N-methylcarbamate (II), was prepared according to the method of Hart[6] and was found to have a boiling point of 70–72° (20 mm). The ultraviolet absorption coefficients of compounds I and II agreed to within 5%. *t*-Butyl acetate was purchased commercially and distilled twice before use.

B. Solid Phase Photolysis. Product characterization and the temperature dependence of ϕ_{II} was achieved in a system which has been previously reported.[1,7]

Uniform polymer films of from 0.4 to 0.8 μ were obtained on quartz microscope slides by dip coating from dilute toluene solutions. Average films weighed from 1 to 2 mg. The solvent was removed from the slides by vacuum drying at 50° for *ca.* 24 hr. Polymer thickness measurements were made with a Watson 16-mm interference objective.

The light source for 2537 Å excitation was a Hanovia 83A-1 low-pressure mercury lamp fitted with both a Corning 7-54 filter and Baird-Atomic 254-mμ interference filter. Above 3000 Å, polymer excitation was accomplished with a GE S-4 100-W mercury arc and a water filter. Spectral purity of the light transmitted in each system was evaluated with a No. 1700-11 Czerny–Turner spectrometer. Lamp intensities were measured with an Eppley thermopile in conjunction with a Hewlett-Packard 3420B DC differential voltmeter.

Photolytic gaseous reaction products were separated and quantitatively analyzed by gas chromatography. Product identification was by infrared spectroscopy following classical microisolation techniques.

C. Liquid Phase Photolysis. All polymer solutions were vacuum degassed five times in quartz cells by the freeze–pump–thaw technique (*ca.* 2×10^{-6} mm) prior to photolysis. Quantum yields at 25° in methanol and 3-methylpentane were determined by the method of Beckett and Porter.[8] The carbonyl absorption band at *ca.* 200 mμ was used to monitor initial rates of disappearance of the carbamate.

Methanol (Baker Analyzed spectrophotometric), cyclohexane (Eastman Spectro Grade), and 3-methylpentane (American Instrument Co.) were used without further purification.

D. Spectroscopy. Ultraviolet and infrared, thin film and solution spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer and Beckman IR-10 infrared spectrophotometer. The temperature dependence of the infrared absorption spectrum of I in film form and $CDCl_3$ (Merck Sharp and Dohme Ltd.) solution was taken using a Limit Research J-1 electrically heated cell. Deuterated chloroform was used because of its transparency in the regions of interest. All infrared measurements were made in matched thickness cells.

Under 2537 Å excitation, phosphorescence spectra and the lifetimes of I and poly(*t*-butyl acrylate) were obtained at 77° K. A Czerny–Turner spectrometer, equipped with an RCA IP-28 photomultiplier tube and Esterline Angus Model S-601-S Speed Servo recorder, was used to measure the emitted light. Phosphorescence lifetimes were obtained by the use of a simple shutter and fast chart speed (3–6 in./sec). Millisecond lifetimes were measured with an Amino-Bowman spectrophotofluorometer with a phosphoroscope attachment and a Tektronix Type 555 dual-beam oscilloscope.

Results

A. Ultraviolet Spectra. A strong similarity in electronic spectral properties of poly(*t*-butyl N-vinylcarbamate in film form and in methanol is shown in Figures 1a and b, respectively. On the other hand, the ultraviolet spectra of I differs with the nature of the solvent. In cyclohexane, a new band emerged at 225 mμ. This transition is partially resolved in Figure 1b. Assuming additivity of optical densities, the absorption had an extinction coefficient of 40 l. mol^{-1} cm^{-1}. An intense band ($\epsilon = 1 \times 10^3$ l. mol^{-1} cm^{-1}) observable at 202 mμ in methanol was blue shifted to 198 mμ in cyclohexane. The third transition in the ultraviolet region was a long wavelength band at 260 mμ. It had an absorption coefficient of 29 l. mol^{-1} cm^{-1}. This band showed a slight red shift from methanol to cyclohexane.

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(2) (a) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **62**, 3375 (1966); (b) E. J. Baum, J. K. S. Wan, and J. N. Pitts, *J. Amer. Chem. Soc.*, **88**, 2652 (1966).

(3) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

(4) G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 188 (1952).

(5) G. O. Schulz and H. James Harwood, Abstracts, Winter Meeting of the American Chemical Society, Phoenix, Ariz., Jan 1966, No. E62; *Polym. Preprints*, 7, 356 (1966).

(6) R. Hart, *Makromol. Chem.*, **32**, 51 (1959).

(7) A. R. Monahan, *J. Polym. Sci., Part A-1*, **4**, 2391 (1966).

(8) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1959).

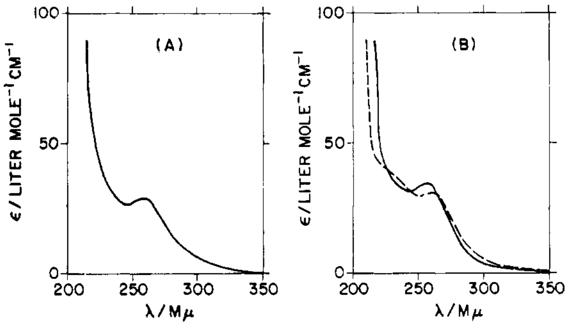

Figure 1. Ultraviolet spectrum of poly(*t*-butyl N-vinylcarbamate) at 25°: (A) 6.4-μ film; (B) ——, 6.90 × 10^{-3} *M* in methanol; -----, 6.90 × 10^{-3} *M* in cyclohexane.

Table I

Quantum Yields for 2537-Å Photoelimination of Isobutene from Poly(*t*-butyl N-vinylcarbamate) Thin Films

Film temp, °C	ϕ_{II}
25	0.01
66	0.01
120 ← T_g	
136	0.02

B. Volatile Products and Thin Film Decomposition. The major volatile products of the 2537 Å photolysis of poly(*t*-butyl N-vinylcarbamate) were found to be isobutene and carbon dioxide. Table I gives the quantum yields for formation of isobutene as a function of temperature. Carbon dioxide and isobutene were found to have identical quantum yields. First-order kinetics were observed by monitoring the formation of these compounds chromatographically in 10-min intervals. Above the glass transition temperature (T_g), a twofold increase in quantum yield was found after correcting for a slight contribution from thermal cycloelimination. The film thicknesses were small enough (~0.5 μ) so that diffusion-controlled rates were not observed at any temperature. Above ~140° the thermal decomposition competed with the photochemical processes and consequently the photolysis temperature range was not extended. The order of magnitude lower yields of isobutane assured that the evolution of isobutene was not from a radical process, *i.e.*, disproportionation of isobutyl radicals.

The formation of a primary amine as a solid product after elimination of isobutene and CO_2 was confirmed by absorption at 1630 cm^{-1}. This was assigned to the NH_2 internal deformation mode.[9] It was observed, using infrared spectroscopy, that the *gauche* ester spatial conformation did not decrease in concentration. This is in marked contrast to the polyacrylate photochemistry[1] (*vide infra*) where a photoinduced rotational isomerization was found to be operative.

A single room-temperature photolysis experiment was carried out using a broad spectral distribution of wavelengths >3000 Å. No product formation was observed even when the total number of quanta absorbed by the 260-mμ transition was equivalent to that absorbed in the 225-mμ band.

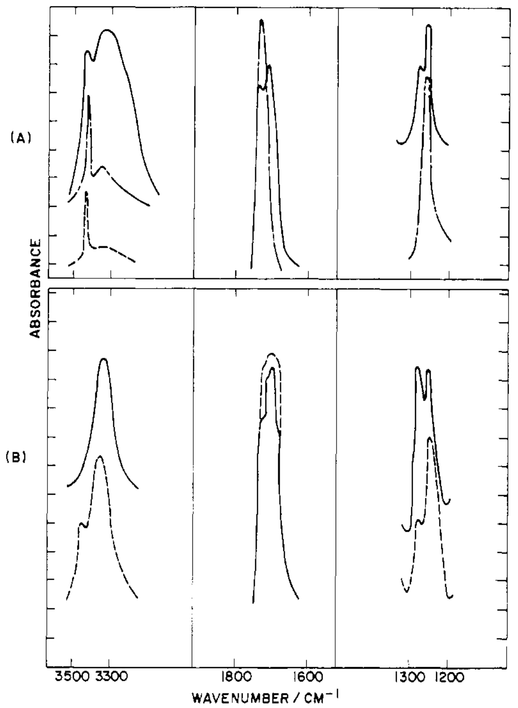

Figure 2. Infrared spectra in N-H, C=O, and C-O regions at 25°: (A) – – –, 0.3 *M* II in CCl_4; ——, 0.3 *M* II in 0.1 *M* ethanol-CCl_4; ----, 0.1 *M* II in CCl_4; (B) ——, II, neat; -----, I, ~1-μ film.

C. Liquid Phase Photochemistry. Quantum yields at 254-mμ excitation for the formation of isobutene and CO_2 from 7.00 × 10^{-3} *M* I in methanol and 1.50 × 10^{-2} *M* I in 3-methylpentane were found to be 0.04 and 0.16, respectively. Photochemical conversions were maintained at ~5% and the yields for the disappearance of poly(*t*-butyl N-vinylcarbamate) were determined spectrophotometrically (*vide supra*) and from gpc analyses of the gaseous products. Solutions had to be degassed as oxygen was found to quench the reaction by *ca.* 50%.

D. Infrared Spectrum and Hydrogen Bonding in the Carbamates. The aforementioned quantum yield results suggested a possible hydrogen-bonding investigation of the pertinent functional groups involved in the photochemistry of I, using infrared spectroscopic techniques. The same types of media were used, *i.e.*, thin films and alcoholic *vs.* hydrocarbon solvents. Portions of the infrared spectra of the model compound (II) in alcoholic and nonpolar media are shown in Figure 2. Also shown is the polycarbamate (I) in film form. Since the monomeric equivalent (II) in hydrogen bonding solvents and poly(*t*-butyl N-vinylcarbamate) were found to show the same spectroscopic band positions and intensities, II was used in the majority of infrared absorption experiments because of the low poly(*t*-butyl N-vinylcarbamate) solubility. The justifications for using CCl_4 as a substitute for hydrocarbon solvents in infrared studies was advanced by Brealey and Kasha[10] in their work on relating hydrogen bonding effects to n-π* blue shifts.

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(9) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p 255.

(10) G. J. Brealey and M. Kasha, *J. Amer. Chem. Soc.*, 77, 4462 (1955).

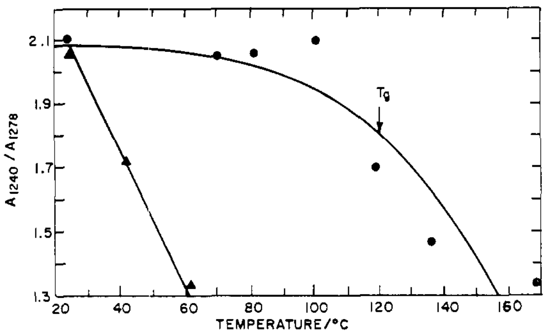
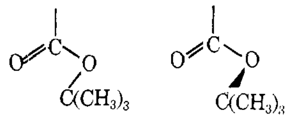


Figure 3. Temperature dependence of the absorbance ratio A_{1240}/A_{1278} for I: ●, 1-μ film; ▲, $CDCl_3$ solution.

The infrared spectrum of 0.3 *M* II in CCl_4 (Figure 2a) was characterized by an intense free N–H band at 3440 cm^{-1} and a lower intensity bonded N–H absorption at 3360 cm^{-1}.[11] The order of intensity in CCl_4 was reversed when 0.1 *M* ethanol was added. The free (1730 cm^{-1}) and bonded (1710 cm^{-1}) carbonyl frequencies were similarly affected. In addition, reduction of the concentration of II from 0.3 to 0.1 *M* resulted in an increase in free N–H at the expense of bonded N–H (Figure 2a). Also, from Figure 2b, compound II in neat form appeared to exist exclusively in a bonded state as noted by the absence of the 3440-cm^{-1} transition.

Bands arising from the different spatial isomers of the ester group were observable in the 1200–1300 cm^{-1} region. The 1240- and 1278-cm^{-1} transitions were previously assigned,[1b,12] in other ester systems, to the C–O vibration of the planar *cis* form and three-dimensional *trans* (*gauche*) isomer, respectively. The relative portions of the two isomers in solution were consistent with conclusions arrived at from dipole moment measurements on carbamates.[13] Interestingly, thin films of II exhibit a greater concentration of the *gauche* rotamer.



cis *gauche*

Previous work on polymeric acrylates[1b] and methacrylates[12] have demonstrated that the *cis* and *gauche* rotamers are interconvertible with heat[1b,12] or light.[1b] The temperature dependence of the absorbance ratio of low energy to high energy isomer of I shown in Figure 3 was essentially the same as for the polyacrylate film. The notable difference between the two systems was that I displayed a temperature dependence of the absorbance ratios in $CDCl_3$ solution whereas the poly(*t*-butyl acrylate) isomer ratio was temperature independent.[1b] In Figure 4, the ratios of bonded to free N–H are shown as a function of film and solution temperatures. Similar to the ester conformational bands, little change in bonding was observed up to the T_g of 120°. Above this temperature, the concentration of free N–H (3440 cm^{-1}) increased quite dramatically. This is pertinent in view of the dramatic increase in ϕ_{II} in this region.

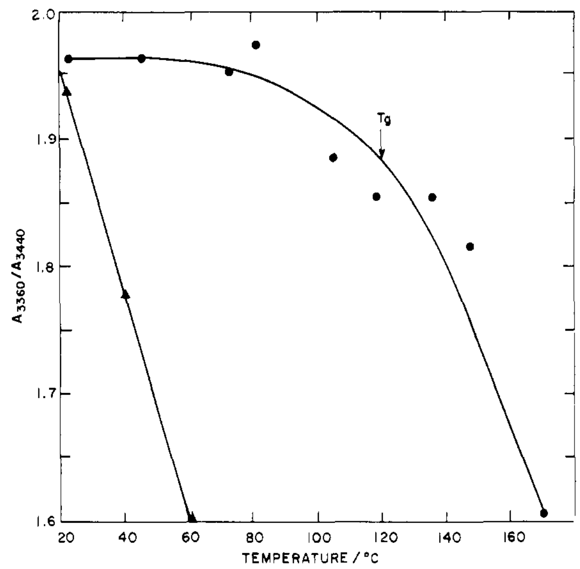


Figure 4. Temperature dependence of the absorbance ratio A_{3360}/A_{3440} for I: ●, 1-μ film; ▲, $CDCl_3$ solution.

E. Phosphorescence of Polycarbamates and Polyacrylates. Previous photochemical studies of ester systems,[1b,2b] as well as this work, show that cycloelimination occurs at least in part from the lowest triplet state of the carbonyl. Hence, any properties of the respective triplet states involved in the work were of value in analyzing the wide variation in ϕ_{II} with structure and solvent properties.

Phosphorescence spectra of the carbamate (I) in 10^{-2} *M* solutions of 3:7 isopropyl alcohol–isopentane and 3-methylpentane were run at 77°K in order to obtain the triplet decay times. Phosphorescence experiments with thin films and solutions of poly(*t*-butyl acrylate) and I provided similar information. The polymer films were obtained by coating inside quartz fingers followed by vacuum removal of the solvent at 50°. The results of these experiments are in Table II. The phosphorescence spectra and lifetimes of I in rigid glass and thin films were identical.

TABLE II
EMISSION FROM THE POLYCARBAMATE AND POLYACRYLATE AT 77°K and 254-mμ EXCITATION

Compound	Medium	0–0 phosphorescence band, mμ	Measured lifetime (τ), sec
I	10^{-2}*M* isopropyl alcohol–isopentane (3:7)	380	4
I	10^{-2}*M* 3-methylpentane	380	0.050–0.100
I	Thin film	380	4
Poly(*t*-butyl acrylate)	Thin film	380	0.050
t-Butyl acetate	10^{-2}*M* isopropyl alcohol–isopentane (3:7)	380	0.015

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[11] See ref 9, p 205.

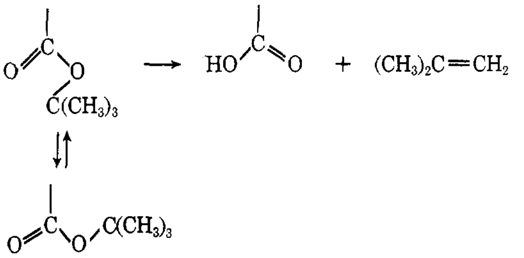
[12] (a) S. Havriliak, Jr., and N. Roman, *Polymer*, **7**, 387 (1966); (b) O. N. Trapoznikova and T. V. Belopdskaya, *Opt. Spektrosk.*, **22**, 974 (1967).

[13] C. M. Lee and W. D. Kumler, *J. Amer. Chem. Soc.*, **83**, 4596 (1961).

Phosphorescence intensities from the polymers were very weak and no detectable fluorescence was observed in either system. The emission spectrum and lifetime[2b] of butyrophenone was used as a calibration standard. Phosphorescence from initiator end groups was not observed as noted by the identical spectra obtained from the model compounds and polymers.

Discussion

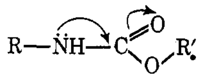
The first long wavelength electronic transition in poly(*t*-butyl acrylate) corresponds to an n–π^* transition.[1a] The absorption band is characterized by an extinction coefficient of 67 l. mol^{-1} cm^{-1} and a bathochromic shift from 212 mμ in methanol to 217 mμ in cyclohexane. The 254-mμ quantum yield for isobutene formation at 25° in thin films was found to be 0.08. An analysis of infrared spectroscopic and kinetic data was consistent with the mechanism



The corresponding details of the poly(*t*-butyl N-vinylcarbamate) photochemistry were analyzed relative to the polyacrylate photolysis. Features of the poly(*t*-butyl N-vinylcarbamate) system worthy of detailed discussion were the wide variations of ϕ_{II} in film form, alcoholic and nonpolar solvents.

The two long wavelength electronic transitions of I at 225 and 260 mμ are assigned to n–π^* excitations of the lone pair electrons on the carbonyl oxygen and nitrogen atom, respectively. The low extinction coefficients (40 and 29 l. mol^{-1} cm^{-1}, respectively), and the absorption band red shifts in cyclohexane relative to methanol were good evidence that this assignment was correct. It was apparent that the lower energy transition belonged to excitation of the lone pair electrons about nitrogen because nitrogen has a lower electron affinity than oxygen.[14] Also, quantum yields were 0.00 when the 260-mμ transition was excited, demonstrating the inactivity of the N atom in the photochemistry of this system. For reasons similar to the assignment of the n–π^* transition, *i.e.*, magnitude of the extinction coefficient and "solvent shift," the 200-mμ band was related to a π–π^* transition.

Excitation of I at 254 mμ in film form gave a ϕ_{II} of 0.01. This is to be compared with a quantum yield of 0.08 for poly(*t*-butyl acrylate). The eightfold lower type II quantum yield was surprising since the polycarbamate n–π^* carbonyl absorbed at a lower energy (225 mμ) than the polyacrylate (215 mμ) n–π^* transition. Substituents that decrease the electron density about a carbonyl oxygen lower the energy of the n–π^* transition and increase the quantum yield for intra- or intermolecular hydrogen atom abstraction. Such interpretations are common through the extensive work by Porter and Suppan[2a,3] and Pitts, *et al.*[2b] Compared with acetates, formates, amides, etc., the carbamates have a lower energy n–π^* state because resonance donating effects, *i.e.* are nonexistent.[15] Thus, the nitrogen acts as an electron-withdrawing group through an inductive effect.



The n–π^* band was hidden beneath the π–π^* band in thin films and alcoholic solution as shown in Figure 1. ϕ_{II} under 254-mμ excitation changed from 0.16 in hydrocarbons to 0.01 and 0.04 in thin films and alcohols, respectively, indicating that the quantum yield decreases were due, at least in part, to a change in the lowest reactive state from n–π^* to a π–π^* character. It is well known that π–π^* states have a larger electron density on the oxygen and subsequently yield a significantly smaller quantum yield for hydrogen atom abstraction.[2b,3] For ease of discussion, only two types of states have been advanced. However, it is well known that mixing of states can occur.[3]

It is well established[2a] that the relative order of states in most carbonyl systems is the same in both singlet and triplet manifolds. Therefore a comparison of the spectroscopically observed states (Figure 1) and any properties of the states derived from low-temperature emission experiments (Table II) was meaningful. The relatively long phosphorescence lifetimes in film form and alcoholic media support a π–π^* type of triplet state whereas the shorter lifetimes for the polyacrylate in film and the polycarbamate in hydrocarbon solvent are indicative of n–π^* transitions. Lifetimes are useful for characterizing such states since a delocalized excited electron and a localized ground state electron,[3] (n–π^*), have a much greater probability to interact and spin flip than a delocalized excited and ground state electron, $^3(\pi-\pi^*)$. Therefore, it is reasonable that $\tau^3(\pi-\pi^*) > \tau^3(n-\pi^*)$.

The change in the nature of the lowest reactive excited state would account for quantum yield variations between the polyacrylate and I in film form and I in hydrocarbon and alcoholic media. However, the strong similarity in absorption and emission properties of I in film form and methanol suggest the lowest reactive state to be of a π–π^* nature in both environments. There is compelling evidence to support a relationship between ϕ_{II} and degree of hydrogen bonding to explain this variation, *i.e.*, as the concentration of N–H $\cdots$ O=C decreases, ϕ_{II} increases. This was shown in Table I and Figure 4 for data on the temperature dependence of the thin film quantum yields and N–H absorbance ratios, respectively. More specifically, hydrogen bonding of the *gauche* rotamer and ϕ_{II} are related in that there is no photorotational isomerization observed. Supporting evidence demonstrating that the *gauche* isomer is preferentially hydrogen bonded was that in the most highly bonded media, *i.e.*, neat film, the *gauche* isomer predominates. It should be em-

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(14) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 452.

(15) T. M. Valega, *J. Org. Chem.*, **31**, 1150 (1966); R. M. Barker, S. L. Vail, and G. J. Boudreaux, *J. Phys. Chem.*, **71**, 2228 (1967).

phasized that in the poly(t-butyl acrylate) system the *trans* form was found to photoisomerize to the *cis* isomer. The spatial conformation of the three-dimensional *trans* isomer (*gauche*) of the ester is such that the t-butylmethyl groups are rotated out of the plane of the carbonyl group[16] leaving the oxygen atom more susceptible to hydrogen bonding. The *cis* isomer cannot hydrogen bond so easily since the methyl groups stagger the carbonyl oxygen. It is apparent that bonding of an intermolecular nature is operative in these carbamate systems. The essential evidence lies in the fact that the (N-H···O=C) bonds are broken upon dilution and the N-H absorbance ratio was temperature dependent in solution.[12a] This is in marked contrast to the polyacrylate system. It is concluded that a dominant factor reducing the type II quantum yield in thin films is due to a releasing of the energy absorbed by the *gauche* isomer *via* some nonradiative process or processes.

Qualitative evidence supporting a relationship between energy dissipation *via* a nonradiative process and hydrogen bonding was advanced by Cowgill[17] in work on fluorescence quenching of tryptophanyl and tyrosyl peptides.

Conclusions

The conclusions may be arrived at by inspection of the data in Table III. The influence of hydrogen bonding on the type II quantum yields from I was found to be dependent on whether the reaction took place in thin films or solution.

In the solution phase experiments, ϕ_{II} decreased from 0.16 in 3-methylpentane to 0.04 in methyl alcohol. A solvent shift causing an inversion of the n–π^* and π–π^* states was also found to occur. Thus, the variation in ϕ_{II} was explained on the basis of a change in electron density distribution in the excited states. Comparisons of the electronic absorption spectra with the phosphorescence lifetimes gave evidence for this interpretation.

TABLE III
COMPARISON OF TYPE II QUANTUM YIELDS FOR THE POLYCARBAMATE AND POLYACRYLATE AT 254-mμ EXCITATION

Compound	Medium	ϕ_{II}	Reactive state
Polyacrylate	Thin film	0.08	n–π^*
Polycarbamate	Thin film	0.01	π–π^*
Polycarbamate	Alcohol	0.04	π–π^*
Polycarbamate	Hydrocarbon	0.16	n–π^*

Second, the significant lower quantum yield of I in film form compared to the polyacrylate film or its yield in alcohol was rationalized on the basis of degradation of the excitation energy *via* some radiationless process occurring from a resonance-stabilized hydrogen bonded *gauche* isomer. Evidence for this was found from infrared studies which showed a photochemically inactive, intermolecularly bonded *gauche* isomer. In addition, ϕ_{II} in thin films was found to increase by a factor of 2 in the temperature region ($>T_g$) where the concentration of N-H···O=C bonds decreased by ~10%.

Therefore, the photochemistry of poly(t-butyl N-vinylcarbamate) appears to be controlled by the subtle interplay of at least two factors: (1) a solvent effect which changes the character of the lowest reactive state and (2) energy degradation *via* hydrogen bonding. Further experiments that will hopefully clarify the mechanism will be the subjects of further investigations.

Acknowledgments. Dr. H. James Harwood of the University of Akron and Miss Anita VanLaeken of this laboratory are sincerely thanked for the syntheses of I and II, respectively. Informative discussions with Drs. J. B. Flannery, D. L. Stockman, and M. S. Walker are acknowledged with pleasure.

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[16] J. M. Riveros and E. B. Wilson, Jr., *J. Chem. Phys.*, 46, 4605 (1967).

[17] R. W. Cowgill, *Biochim. Biophys. Acta*, 133, 6 (1967).

Photochemistry of Ketone Polymers.
II. Studies of Model Compounds

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ABSTRACT: Studies of the photolysis of model ketones of the general structure R(C=O)R in hydrocarbon solution show that the type I and type II quantum yields are functions of chain length. The type I quantum yield decreases rapidly, and reaches a limiting value of 0.012. The type II quantum yield decreases slowly and appears to be still decreasing in ketones containing about 40 carbon atoms, where it has a value of 0.06. Although the type II process is insensitive to temperature and solvent viscosity, the type I process depends strongly on both, as might be expected from a process involving radical intermediates. The results of these studies indicate that the photochemistry of the largest of the model compounds is quite similar to that of the ketone polymers studied previously.

In a previous publication[1] we have described the photochemistry of polymeric ketones synthesized by the copolymerization of ethylene and carbon monoxide. At an early stage in the investigation it became apparent that variations in the molecular weight of the polymer had very little effect on the quantum yields of the processes involved, and yet there was a marked difference between these yields and those for the relatively small organic molecules reported in the literature. It therefore became of interest to establish the molecular

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[1] G. H. Hartley and J. E. Guillet, *Macromolecules*, 1, 165 (1968).