Macromolecules 1988, *21*, 1165–1169 **1165**

pendences of dye diffusion in polyisoprene–THF solutions with moderate success, yet marginally hold for the polystyrene–THF solutions.

Finally, we were unable to test the Vrentas–Dudas model against that of Fujita with respect to the *temperature* dependence of probe molecule diffusion. However, the models of Vrentas and Duda and of Fujita have used expressions which can be related to the WLF method; therefore we examined the temperature dependence with the WLF format. Parenthetically we should add that the simpler Fujita free volume theory coupled with the WLF equation was shown to suffice[24] in accounting for the temperature dependence of polymer self-diffusion coefficients through the monomer friction coefficient ζ_0.

Acknowledgment. This work was in part supported by the National Science Foundation (Polymers Program) and the Kodak Research Laboratories. We also acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are most grateful to Prof. Icksam Noh for synthesizing one of the polyisoprene samples during his stay in our laboratory.

Registry No. PS, 9003-53-6; PI, 9003-31-0; methyl red, 493-52-7; methyl yellow, 60-11-7.

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On the Cross-Linking Mechanism of Benzophenone-Containing Polyimides

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ABSTRACT: A group of fully imidized polyimides containing benzophenone as well as alkyl-substituted biphenylmethane in the main chain were prepared. In these materials cross-links are formed on exposure to UV radiation through hydrogen abstraction by triplet benzophenone from the alkyl groups acting as hydrogen donors and subsequent coupling of the radicals so formed. The involvement of radicals in the process is supported by the ESR spectra of the films under irradiation. The quantum yield of cross-linking is $\phi = 0.027$, and less than half of the benzophenone units in the solid are reactive. Even at the reactive sites the reaction probability is a mere 3%. The low quantum efficiency in the solid state of a reaction which in solution proceeds with high yield is attributed to a specific energy dissipation process, which operates at the reactive site in the solid state, namely, reversible hydrogen exchange between benzophenone and the hydrogen donor.

The increasing importance of polyimides in the manufacture of integrated circuits has motivated numerous investigations on the development of photoimageable polyimides. The objective here is to produce polymers that can be exposed and processed like a photoresist but which are sufficiently stable, thermally and mechanically, to be

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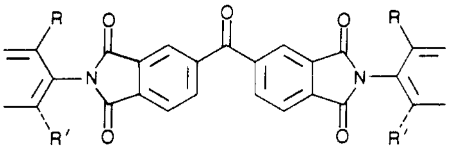
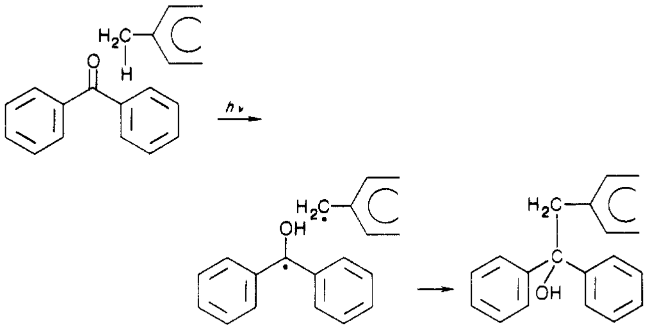
incorporated as permanent components into electronic devices. Systems developed and evaluated in recent years have been reviewed[1] and reports on new approaches continue to emerge.[2-4]

In most instances the new designs entail the introduction of photosensitive groups into known polyimide precursors. The esterification of polyamic acids with polyfunctional derivatives of allylalcohol[5,6] is an example. All of these materials suffer from a serious deficiency: they shrink in the imidization step following exposure and development. A fully imidized, solvent-soluble polyimide system recently reported by Pfeifer and Rohde[7] overcomes this difficulty. The polymer combines thermal and mechanical stability with good image resolution, reasonable photospeed, and simple processing. It has become one of the most important imaging materials of microelectronics and its lithographic properties have been described. The operative part of the polymer structure was indicated by the formula



I

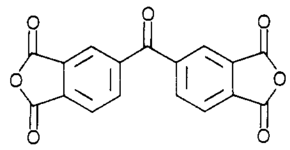
and the statement was made[7] that "the chemical pathway of the photocross-linking mechanism is completely unknown". We have been interested in photocross-linking mechanisms for some time and, looking at structure I, thought that cross-linking could well proceed through hydrogen abstraction by triplet benzophenone and subsequent coupling of the radicals so formed. The present paper describes experiments which were undertaken to test this hypothesis.



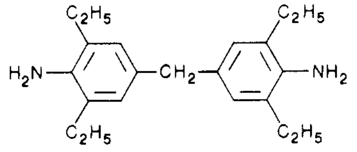
Cross-linking by radicals photogenerated via triplet benzophenone is not without precedent: hydrogen abstraction from suitable hydrogen donors by an excited benzophenone molecules is one of the classical reactions of organic photochemistry[8,9] and a whole class of industrial photoinitiators (i.e., radical generators) is based on hydrogen exchange between aromatic compounds and hydrogen donors.

Oster et al. have reported as early as 1959[12a] that benzophenone is able to cross-link vinyl polymers on irradiation; Smets et al.[12b] have shown that copolymers of vinylbenzophenone and 4-(dimethylamino)styrene cross-link by a radical coupling mechanism. More recently, Horie et al.[13] have observed the photoreaction of benzophenone in solid films of poly(vinyl alcohol).

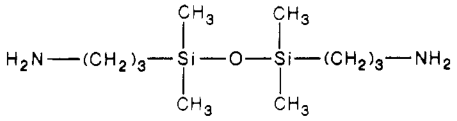
To investigate the involvement of benzophenone and of hydrogen donors in the cross-linking of the polyimides described by Pfeifer and Rohde,[7] we prepared a group of block copolymers from the following components: 3,4;3',4'-Benzophenonetetracarboxylic dianhydride (BTDA) is the presumed photoreactive entity, the hydrogen or electron acceptor. Tetraethylmethylenedianiline (TEMDA) carries the ethyl groups which are thought to act as hydrogen donors. 1,3-Bis(aminopropyl)tetramethylsiloxane (BADS) is an alternative diamine component which may replace TEMDA but does not function as a hydrogen donor.[14]



BTDA



TEMDA

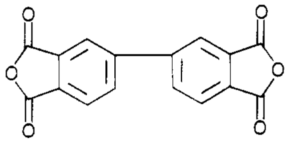


$H_2N{-}(CH_2)_3{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}(CH_2)_3{-}NH_2$

BADS

Polyimide block copolymers were prepared with varying proportions of TEMDA and BADS, and the photoreactivity of the copolymers was evaluated by determining their gel dose, i.e., the radiation dose required for incipient gel formation.

To demonstrate the role of benzophenone in these systems, a copolymer was prepared in which the benzophenone moiety was replaced by biphenyl-3,4;3',4'-tetracarboxylic dianhydride (BPDA).



BPDA

The progress of the photoreaction was followed by monitoring the changes in the IR spectrum of the polymer during irradiation. The presence of free radicals in the irradiated films was demonstrated by ESR spectroscopy.

Experimental Section

Preparation and Characterization of Polymers. Block copolymers were prepared from BTDA and the amine monomers. A random copolymer was included to probe the effect of the juxtaposition of reactive groups in the photochemical reaction.

Tetraethylmethylenedianiline (TEMDA) was supplied by Ethyl Corporation, bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (BADS) by Petrarch, and *s*-biphenyl dianhydride (BPDA) by Chriskev. All were used as received. Benzophenonetetracarboxylic dianhydride (BTDA, Aldrich) was recrystallized from acetic anhydride and dried at 150 °C in a vacuum oven before use. Dry dimethylacetamide (DMAc, Aldrich) and other solvents were used as received.

The procedure for the preparation of the block copolymers was as follows: recrystallized dianhydride (0.01 mol) was accurately weighed into a round-bottom flask and dissolved in 50 mL of dry *N,N*-dimethylacetamide (DMAC) at room temperature. The specified amount of TEMDA was added and the solution was stirred for 1 h under nitrogen. A solution of the amine comonomer required for a total of 0.1 mol of diamine in DMAC was then added dropwise and stirring was continued at room temperature for 4 h, under nitrogen. For the imidization of the polyamic acid, 7 g of fused sodium acetate and 15 g of acetic anhydride were added and the mixture was then heated in an oil bath at 85 ± 3 °C for 2 h. After cooling, the mixture was poured into ice water. The

Table I
Characteristics of the Block Copolymers

	mole ratio TEMDA/BADS, %	M_0,[a]	T_g, °C[b]	yield, %
II	100:0	26 000	270	85.5
III	80:20	30 000	216	81.8
IV	50:50	21 000	147	70.4
IV[c]	50:50	21 000	133	91.8
V	20:80	21 000	93	90.3
VI	0:100	18 000	67	61.7
VII	50:50	23 000	138	96.2

[a] GPC on microstyragel; THF, 0.8 mL/min. [b] DSC under nitrogen; heating rate 10 deg/min. [c] Random copolymer.

Table II
Effect of H-Donor Content on Gel Dose

		gel dose, mJ/cm^2		
polymer	TEMDA:BADS	air	nitrogen	oxygen
II	100:0	26.0	23.2	34.7
III	80:20	34.7	26.0	40.8
IV	50:50	66.5	60.7	75.2
IV[a]	50:50	75.2	72.2	81.0
V	20:80	150	148	159
VI	0:100			

[a] Random copolymer.

solid which precipitated was filtered off, washed with dilute Na_2CO_3 solution, water, and methanol, and then dried. The polymers were dissolved in THF, reprecipitated with methanol, and again dried before characterization.

The random copolymer was prepared by mixing all reactants and reacting for a total of 5 h at 85 °C. Analytical data (IR, NMR), molecular weights, and T_g are summarized in Table I. All polymers were soluble in THF, DMAC, and dichloromethane.

DSC scans were run on a Du Pont 910 cell interfaced with a Du Pont 1090 thermal analyzer. Scans were run under nitrogen at a heating rate of 10 °C/min.

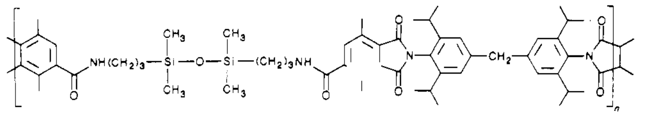
GPC analyses were carried out on a Waters GPC 1 Model 590 chromatograph, using 10^4, 10^3, and 500 Å microstyragel columns in series. THF was the eluent at a flow rate of 0.8 mL/min. The instrument was calibrated with a set of polystyrene standards.

Emission spectra were taken with a Perkin-Elmer Model II instrument. The samples were presented in a quartz tube, immersed in a Dewar vessel filled with liquid nitrogen.

The photoreactivity of the polymers was measured in terms of their gel dose.[15] The films were exposed to the output of a monochromator-xenon arc combination (Bausch and Lomb). The source was calibrated by ferrioxalate actinometry, and the gel dose, D_G (in mJ/cm^2), was determined. These data are listed in Table II.

Results and Discussion

The Role of Benzophenone and of the Hydrogen Donors. The potential involvement of the benzophenone moiety in the cross-linking of I was indicated by the results of a simple preliminary experiment. The photoinsensitive polymer VIII, made by a method described in ref 16, was



VIII

doped with up to 20 wt % benzophenone, coated from solution on a glass slide, dried, and gradually exposed to a Hanovia mercury vapor lamp. After exposure the material was scraped off the glass, dissolved in THF and injected into a GPC column. The benzophenone peak initially present in the chromatogram rapidly decreased on exposure of the solid film (see Figure 1) as benzophenone was grafted onto the polymer. These results demonstrate that photoexcited benzophenone is able to react with some constituents of polymer VIII.

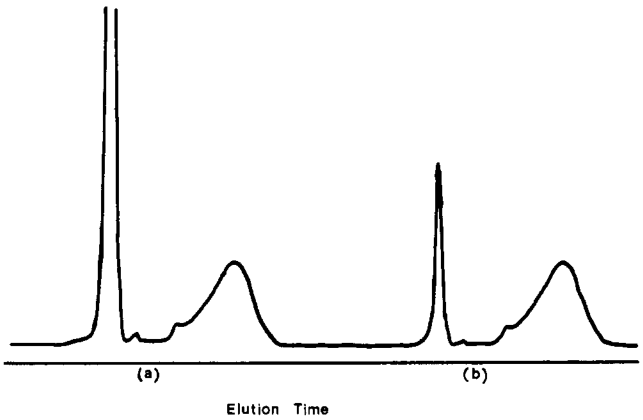


Figure 1. Gel permeation chromatogram of a film of polymer VIII containing 20 wt % benzophenone, (a) before and (b) after 15 min exposure to a Hanovia mercury lamp.

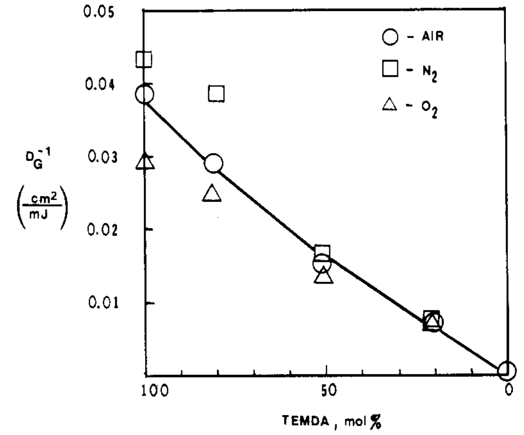


Figure 2. Effect of TEMDA content on the reciprocal gel dose (in mJ/cm^2) of a group of polymers with TEMDA:BADS ratios varying from 1 to 0: exposed in air (○); in nitrogen (□); in oxygen (△).

Confirmation of the role of the hydrogen donors, i.e., the alkyl groups of the diamine moiety, is provided by the results obtained with the copolymers II to VI listed in Table II. The data plotted in Figure 2 in terms of sensitivity (reciprocal gel dose, cm^2/mJ) show that the photoreactivity is an almost linear function of the hydrogen donor (TEMDA) content of the polymer. This is strong confirmation of our hypothesis.

Inhibition by Oxygen. The exposure experiments described above were carried out in air, nitrogen, and oxygen, and it can be seen from the data in Figure 2 that there is a small oxygen inhibition effect. This is in contrast to other cross-linking or photopolymerization systems where oxygen completely inhibits the photoprocess. Pfeifer and Rohde[7] have stressed the absence of oxygen inhibition in their materials, because this is an important advantage in practical lithography. Smets et al.[12] have interpreted the absence of an oxygen effect in benzophenone–(dimethylamino)styrene copolymers by the formation of electron donor–acceptor complexes. Since the reaction sequence takes place in a single locality, exciplex formation and the subsequent steps compete very effectively with oxygen quenching.

A similar argument applies in our polymers, but there is a difference: the dimethylamino group of Smet's systems is replaced by phthalimide which is not an electron donor and cannot form electron donor–acceptor complexes with benzophenone. In contrast, the phthalimide group is a mildly electron-withdrawing substituent and will enhance

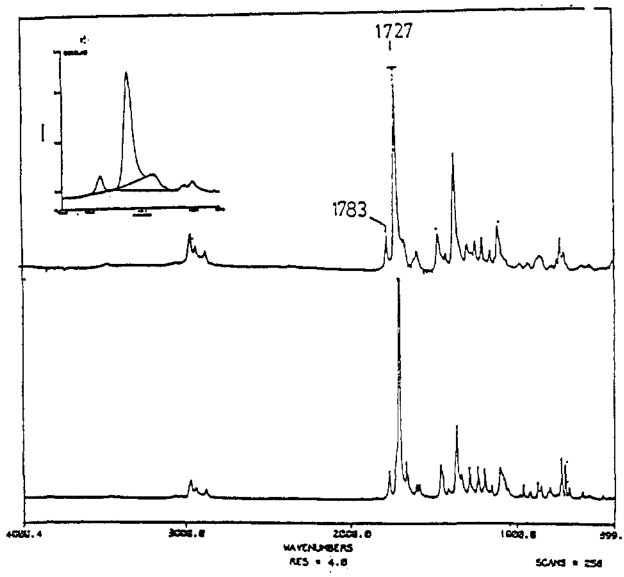


Figure 3. FTIR spectrum (256 scans) of polymer II. Inset: enlarged plot of C=O absorption at 1727 cm^{-1} and the phthalimide mode at 1783 cm^{-1}.

the acidity, i.e., the hydrogen donating tendency of the ortho- or para-positioned alkyls on the adjacent phenyl ring. This is in agreement with the observations of Pfeifer and Rohde[7] who found that alkyl groups in the meta position relative to phthalimide lead to less photoreactive polymers.

Involvement of Phthalimide Carbonyls. The carbonyl group of benzophenone is only one of five carbonyl groups in the BTDA moiety of the polymer. The carbonyls of the phthalimide nuclei are known to be photoreactive and their involvement in cross-linking has to be considered. Kanaoka has investigated the photochemistry of phthalimides and has shown that it is dominated by intramolecular cyclization reactions which cannot contribute to intermolecular cross-linking.[17-19] This expectation was confirmed for our polymers by an experiment where a copolymer (VII) was prepared containing both the phthalimide carbonyls as well as the hydrogen donors of TEMDA, but not the benzophenone. This polymer did not cross-link even after prolonged irradiation (1 h). The phthalimide carbonyls do not contribute to cross-linking.

The Quantum Yield of Cross-Linking and the Degree of Completion of the Photoreaction. The quantum yield of cross-link formation, ϕ, was derived from the gel dose, the weight-average molecular weight, M_w, the molarity, m_B, of BTDA in the solid film, and its extinction coefficient, e_B, at wavelength of irradiation, 310 nm.[15]

$$\phi = [2.303 m_B e_B M_w D_g]^{-1}$$

With m_B = 1.67 mol/L, $e_B = 5.41 \times 10^3$ L/(mol cm), M_w = 26.000, and D_G (at 310 nm) = 26.0 mJ/cm^2 = 6.73×10^{-8} einstein/cm^2, this leads to a value for the quantum yield of cross-link formation of ϕ = 0.027. The value of D_G is in good agreement with the work of Pfeifer and Rohde who report for one of their polymers a gel dose of 20 mJ/cm^2.)

The degree of completion of the benzophenone photoreaction in the solid depends on the fraction of reactive benzophenone sites, i.e., of sites where benzophenone and a hydrogen donor are within reach of each other. The fraction of reactive sites can be estimated by monitoring, during exposure, the change in the concentration of unreacted benzophenone groups by IR spectroscopy.

The polymer was coated in the form of a thin film on a KBr disk and the IR spectrum was taken on a Digilab FTIR spectrometer. The spectrum is shown in Figure 3.

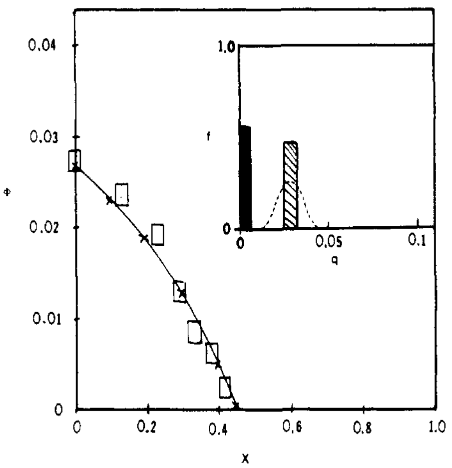
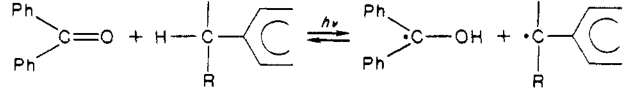


Figure 4. Quantum yield versus degree of benzophenone conversion; the solid line is calculated for a constant site reactivity of 0.03.

The strong absorption at 1727 cm^{-1} corresponds to the stretching vibration of all five carbonyl groups in the BTDA moiety. The weak line at 1783 cm^{-1} is assigned to a deformation mode of the five-membered heterocyclic ring of phthalimide. It does not change on irradiation and can therefore be used as an internal calibration standard. The progress of the photoreaction is measured by the disappearance of that part of the C=O absorption which belongs to the benzophenone carbonyl. From the data the quantum yield of the photoprocess as a function of the degree of benzophenone conversion can be derived.[20] Figure 4 is a plot of quantum yield versus the degree of conversion. The inset in the figure is a histogram of the distribution of site reactivities, which indicates that only 45% of all benzophenone sites are reactive and that all reactive sites have approximately the same reaction probability, namely, 0.03 per excitation event. The solid line of the $\phi(x)$ function in Figure 4 was calculated for this simple bimodal histogram and it can be seen to represent the experimental results reasonably well. In a more realistic histogram the single bar at the reaction probability of 0.03 is replaced by a narrow Gaussian distribution, as indicated by the broken line in the figure.

Two aspects deserve comment: the total nonreactivity of over 50% of the benzophenone units and the low quantum yield of cross-link formation in the solid, when in solution the photoreduction of benzophenone, e.g., by (dimethylamino)toluene, has a quantum yield of 0.35. Both effects are caused by the fixed positions of the reactants. In the solid matrix a substantial fraction of benzophenone carbonyls are not within reach of a hydrogen donor. Furthermore, we believe that in these conditions hydrogen exchange between benzophenone and the alkyl group of the hydrogen donor is reversible and that this provides a mechanism for the radiationless deactivation of the excited state.



One recalls a similar mechanism for the dissipation of electronic energy in the 2-alkyl-substituted benzophenones, where a transient and reversible intramolecular isomerization (hydrogen exchange) process prevents hydrogen abstraction from the solvent.[21,22] Similarly, 2-hydroxy- or 2-amino-substituted benzophenones do not phosphoresce in solid solution at 77 K,[23] because the radiative transition is overwhelmed by the nonradiative (hydrogen exchange)

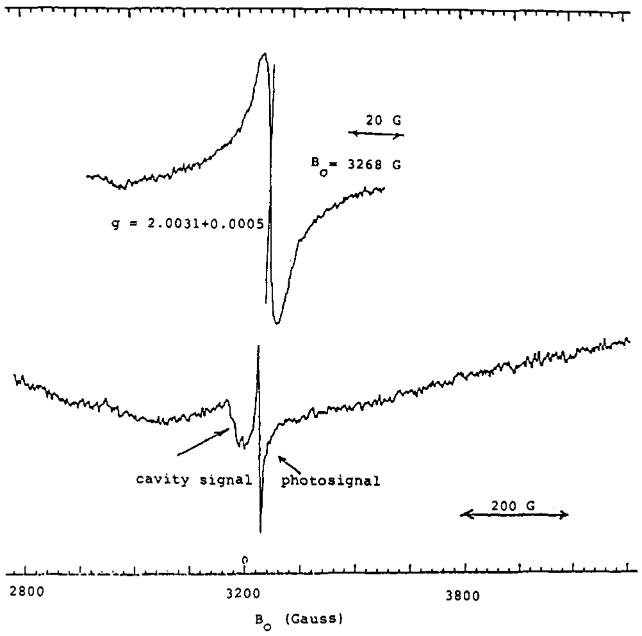


Figure 5. ESR spectrum of polymer II, exposed to 365-nm radiation at 20 K. A strong radical signal is located at 3268 G; $g = 2.0031 \pm 0.0005$.

deactivation process. Reversible hydrogen exchange between excited benzophenone and the hydrogen donor is a plausible explanation for the low efficiency of cross-link formation at the reactive sites of our polymers.

ESR Measurements. ESR spectra of the polymers under irradiation were taken with a Varian E-12 Century Series spectrometer operating at 9.16 GHz. The instrument was fitted with a Heli-Tran helium cryostat (Air Products Ltd) and with a Lake Shore Cryotronics Model DRC-81C controller.

Thin film strips 3 mm wide of the samples were placed in a quartz ESR sample tube. The samples were handled under dim red light at all times. Once in the ESR cavity they were exposed to 365-nm radiation from an SP-200 super pressure mercury arc passed through a Bausch and Lomb monochromator and an interference filter.

Figure 5 shows a typical ESR spectrum obtained at 20 K with polymer II (100% TEMDA). At 30-mW microwave power this polymer gave a strong single narrow ESR line at 3268 G ($g = 2.0031 \pm 0.0005$), indicating the presence of a free radical (doublet state). The same signal was generated with polymer IV (50% TEMDA) in the cavity, but at about half the intensity of sample II. In polymer VI (0% TEMDA) the signal could not be detected. The strength of the ESR signal which measures the free radical content in the photostationary state was found to be approximately proportional to the TEMDA (i.e., hydrogen donor) content of the material. Since the same proportionality is observed for the degree of cross-linking, it is concluded that the cross-links are mediated by free radicals.

In the amorphous polymeric solid the spectra have no hyperfine structure and the identity of the free radical cannot therefore be assigned from the spectrum. The position and general shape of the signal is compatible both with the ketyl radical and with the alkyl free radical of the TEMDA moiety of the irradiated polymer.

Conclusion

The hypothesis that in the group of polyimides investigated cross-linking is brought about through hydrogen abstraction by excited benzophenone and through subsequent radical coupling conforms to all our observations.

1. Polymers which do not contain the benzophenone unit do not cross-link on exposure, neither do polymers which contain benzophenone but lack hydrogen donors.
2. The photosensitivity (reciprocal gel dose) of polymers with the same benzophenone content is proportional to the content in hydrogen donors in the material.
3. The dependence of the quantum yield of the photoreaction on the degree of benzophenone conversion indicates that not more than 45% of benzophenone is located at reactive sites and that the efficiency of cross-link formation at these sites is low, on the order of 0.03. Reversible hydrogen exchange between benzophenone and the hydrogen donor is a plausible explanation for this low reaction probability.
4. There is only weak inhibition of cross-linking by oxygen, suggesting that at the reactive sites the carbonyl group of benzophenone and the alkyl groups of the hydrogen donor are so juxtaposed that hydrogen transfer competes effectively with quenching by oxygen.
5. The involvement of free radicals in the cross-linking process is unequivocally demonstrated by the ESR spectra of free radicals in the photoactive polymers and the absence of an ESR signal in the inactive ones.

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Registry No. (BTDA)(TEMDA) (copolymer), 96211-30-2; (BTDA)(TEMDA) (SRU), 96126-69-1; (BTDA)(TEMDA)(BADS) (block copolymer), 113180-80-6; (BADS)(TEMDA) (copolymer), 30679-44-8; (BADS)(TEMDA) (SRU), 32126-24-2.

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