has been developed. The model is based upon the detection and identification of four types of water incorporated in cellulose: (1) primary bound; (2) secondary bound; (3) free; and (4) bulk.

2. A point of plasticization has been associated with the transition between primary bound and secondary bound water, and is associated with swelling of the structure allowing increased mobility of the cellulose chains.

3. Free water has been shown to exist at very low moisture contents with the amount of free water increasing dramatically above the point of plasticization. This says in effect that although the adsorption process involves different types of water at different relative humidities it is a combined process involving free water.

4. The primary implication of these results is that the incorporation of specific types of sorbed water will lead to dramatic changes in physical properties. From the results obtained one might expect large changes in the physical properties of the material above the point of plasticization. One would also expect the point of plasticization to depend on the material studied since the accessibility would vary.

References and Notes

(1) E. Filby and O. Maass, *Can. J. Res.*, **7**, 162 (1932).
(2) A. Champetier, *C. R. Hebd. Seances Acad. Sci.*, **195**, 280 (1932); **195**, 499 (1932).
(3) A. J. Stamm and W. K. Loughborough, *J. Phys. Chem.*, **39**, 121 (1934).
(4) F. C. Magne, H. J. Portas, and H. J. Wakeham, *J. Am. Chem. Soc.*, **69**, 1896 (1947).
(5) F. C. Magne and E. L. Skau, *Text. Res. J.*, **22**, 748 (1952).
(6) J. Ayer, *J. Polym. Sci.*, **21**, 455 (1956).
(7) J. L. Neal and D. A. Goring, *J. Polym. Sci.*, **628**, 103 (1969).
(8) Y. Ogiwara, M. Kubota, S. Hayashi, and N. Mitomo, *J. Appl. Polym. Sci.*, **13**, 1689 (1969); **14**, 303 (1970).
(9) M. Sasaki, A. Tikawa, A. Hirai, T. Hashi, and A. Odajima, *J. Phys. Soc. Jpn.*, **15**, 1652 (1960).
(10) T. F. Child, *Polymer*, **13**, 259 (1972).
(11) J. Carles and A. Scallan, *J. Appl. Polym. Sci.*, **17**, 1855 (1975).
(12) R. Stratton, *J. Polym. Sci.*, **11**, 535 (1973).
(13) C. E. Boesen, *Cellul. Chem. Technol.*, **4**, 149 (1970).
(14) E. L. Hahn, *Phys. Rev.*, **80**, 580 (1950).
(15) J. A. Howsmon, "High Polymers", Vol. 5, E. Ott, H. Spurlin, and M. Grafflin, Ed., Interscience, New York, N.Y., 1954, p 393.
(16) N. Bloombergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 697 (1948).
(17) S. Seitsonen and I. Middonen, *Polym. J.*, **5**, 263 (1973).
(18) T. Swanson, E. V. Stejskal, and H. Tarleow, *Tappi*, **45**, 929 (1962).

N(1s) X-Ray Photoelectron and Electronic Absorption Spectra of Poly(squarylamides)

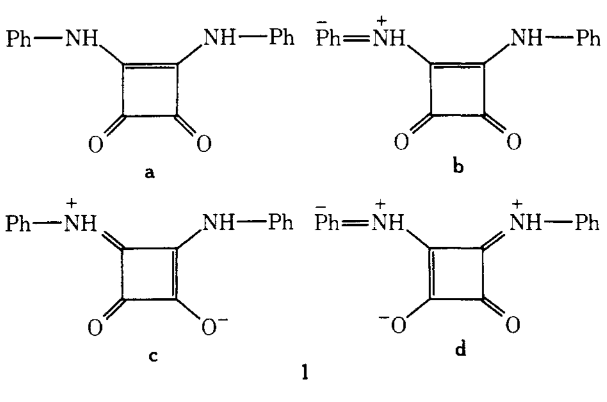
Eberhard W. Neuse,*[1a] Brian R. Green,[1a] and Reiner Holm[1b]

Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa, and Bayer AG, Leverkusen, Germany.

Received March 3, 1975

ABSTRACT: The products of polycondensation of *p*-phenylenediamine with either squaryl dichloride or squaric acid obtained in preceding work, containing either the 1,2-disubstituted or the isomeric 1,3-disubstituted cyclobutene ring system in the recurring unit, are investigated by X-ray photoelectron and electronic absorption spectroscopy. The findings are in agreement with highly delocalized electronic systems and indicate more than 50% iminium character in both polymer types. The cyclobutene-3,4-dione and cyclobutenediylium 2,4-diolate structures, respectively, employed previously for description of the four-membered ring moieties in the two polyamide isomers cannot, therefore, be regarded as valid structural representations, although the use of these and other structures with formally uncharged nitrogen atoms may be retained for convenience of drawing.

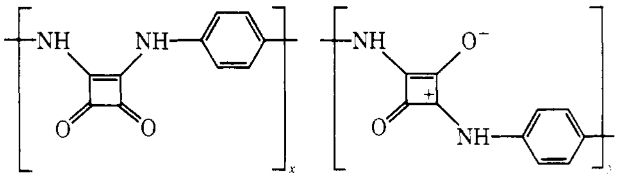
A recent study[2] of the two isomeric dianilides of squaric acid, **1** and **2**, by electronic and X-ray photoelectron (ESCA) spectroscopy has revealed some rather striking structural features. In **1**, the spectroscopic data point to canonicals **b–d** as major ground-state contributors, whereas the 1,2-dianilinocyclobutene-3,4-dione structure **1a**, commonly accepted to that day as a valid description, in fact represents but a minor contributing form. In **2**, forms **c–e** are important, while **2a** and **2b**, both proposed as predominant canonicals in the earlier literature, carry minor weight in the hybrid. It is thus evident that both dianilides represent highly mesoionic systems possessing considerable iminium character.



1

It is instructive to compare the charge distributions in these nonpolymeric amides with those in analogous polymeric squaryl amides of the types **3** and **4**.[3] These polyamides, in keeping with common terminology in squaric acid chemistry,[4] were depicted in the quoted communications[3] by the dione and diolate structures **3a** and **4a**, respectively.[5] In view of the predominance of iminium structure in **1** and **2** it stands to reason, however, that the representations **3a** and **4a** do not reflect the actual distribution of charge in these polymers. In an effort to clarify the problem of charge distribution and assess the relative thermal stability behavior resulting from potentially different extents of

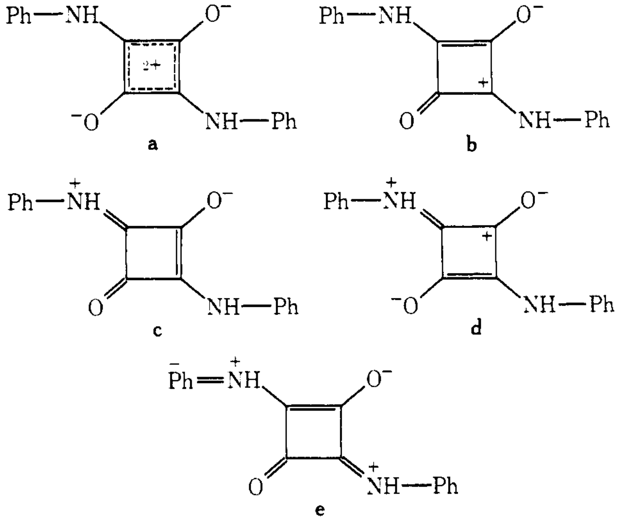
Table I
Electronic Absorption Maxima, N(1s) Binding Energies, and Nitrogen Atom Charges of Some Amino Derivatives of Squaric Acid



3-4

Compd	λ_{max}, nm[a]	E_b, eV: ES 200[b]	E_b, eV: Du Pont 650[c]	E_b, eV: Ultimate value[d]	q_N[e]
5	255 sh 287				
6	260 293				
1a	305 340 sh			399.5	0.02
2b	368			399.6	0.04
3a	400	399.6	399.4	399.55	0.03
4b	500	399.6	399.5	399.6	0.04
3–4 ($x \approx y$)[f]	450				

[a] In KBr matrix. Values for 1, 2, 5, 6 taken from ref 2. [b] With Al Kα radiation. Spectra calibrated separately against $NaNO_3$ and NH_4NO_3 (three scans with each standard; E_b values averaged). Precision, ±0.2 eV; estimated accuracy, ±0.7 eV. [c] With Mg Kα radiation (two scans; E_b values averaged). Precision, ±0.1 eV; estimated accuracy, ±0.5 eV. [d] Average of values from two preceding columns, each weighted by number of scans and rounded to one decimal place. Values for 1 and 2 taken from ref 2. [e] From E_b of preceding column by means of Siegbahn's correlation (ref 9a); precision, ±0.04. [f] Random sequence implied.



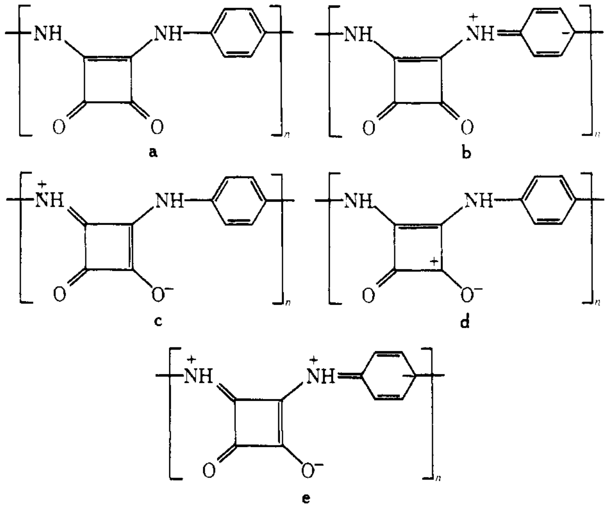
2

electronic delocalization, we investigated representative polymers of both types 3 and 4 by electronic absorption spectroscopy, X-ray photoelectron spectroscopy (ESCA), and thermogravimetric analysis (TGA).

Results

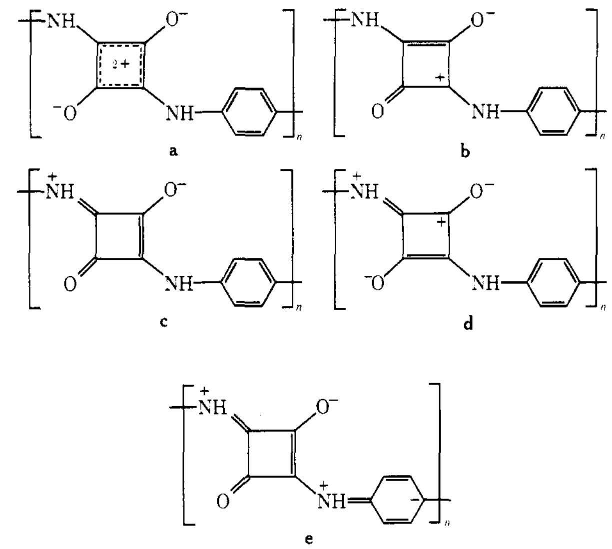
The poly(squarylamides) were prepared by the techniques described,[3d] involving polycondensation of squaryl dichloride with *p*-phenylenediamine, to give a polymer substantially of structure 3, and polycondensation of squaric acid with the same diamine in a basic medium, to yield polymer product essentially of structure 4.[6] In addition, a polyamide of intermediate composition, labeled 3–4, was synthesized from squaric acid and diamine in an acidic medium.

Electronic spectra of 3, 4, and 3–4 contained as "solutes" in KBr disks were recorded in the 300–550 nm region representing $\pi \rightarrow \pi^*$ transitions of the anilino–enone (or anilino–enolate) system.[2,7] The KBr embedding technique, while disallowing a quantitative intensity assessment because of interfering base line variation, offers the benefit of providing maxima that reflect the true solid-state structure of the substrate unperturbed by protonation effects arising in acid solvents.[8] The maxima recorded are listed in Table I.

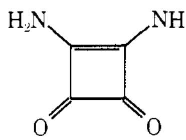


3

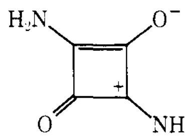
The ESCA spectra were taken on solid samples of 3 and 4 as in the previous work.[2] N(1s) binding energies, $E_{\mathrm{b}(3)}$ and $E_{\mathrm{b}(4)}$, were derived from spectra recorded on a precalibrated instrument and were independently obtained by calibration against both $NaNO_3$ and NH_4NO_3; the results were then averaged. The binding energy values of the three types of nitrogen in the reference compounds were taken from the literature ($E_{\mathrm{b(Na}N\mathrm{O_3)}}$ = 407.2 eV;[9a] $E_{\mathrm{b(}N\mathrm{H_4NO_3)}}$ = 402.3 eV;[9b] $E_{\mathrm{b(NH_4}N\mathrm{O_3)}}$ = 407.2 eV[9c]). The values for $E_{\mathrm{b}(3)}$ and $E_{\mathrm{b}(4)}$ thus determined, as well as the corresponding nitrogen atom charges, q_N, taken from Siegbahn's correlation,[9a] are given in Table I. The respective λ_{max}, E_b, and q_N data obtained in the previous investigation[2] on the nonpolymeric model compounds 1 and 2 are relisted in the table for comparison, as are the electronic absorption maxima for the unphenylated diamides 5 and 6.



4



5



6

TGA thermograms of **3**, **4**, and **3–4** were recorded in Ar atmosphere at a heating rate of 6° $\min^{-1}$. The temperature ranges of incipient weight loss are given in Table II along with the relative residual weights at 600, 700, 800, and 900°.

Discussion

The structural representations **3a** and **4a** imply sp^3 hybridization of both nitrogen atoms. Predominance of these forms in the resonance hybrids of the two polyamide types should hence afford the same chromophores as exist in the simple diamides **5** and **6**. The tabulated $\lambda_{\max}$ data show this by no means to be the case. Both **3** and **4** (as well as **3–4**), on the contrary, give maxima substantially red-shifted not only relative to the unphenylated model compounds **5** and **6**, but even in relation to the dianilides **1** and **2** shown earlier[2] to include the anilino groups in their chromophores. Both polymer types, and likewise the polyamide of intermediate composition, clearly possess domains of π conjugation more extended than found in **1** and **2** and thus must comprise in their chromophores the *p*-phenylene in addition to the cyclobutenedione ring systems in substantially coplanar alignment. As this can be brought about only by participation of sp^2-hybridized N, canonicals of the amine type (**3a**, **4a,b**) clearly carry little weight. Instead, one must assume appreciable iminium character in both polymers, an inference borne out by the tabulated ESCA results. The nitrogen atom charges, q_N, of **1**, **2**, **3**, and **4** are all found to be identical within experimental error limits[10] and so allow the assignment of ca. 60% iminium structure[11] to the polymer. In **3**, the algebraic mean of the (asym and sym) C–O stretching bands[12] (1731 cm^{-1}) practically coincides with that in squaric acid (1732 cm^{-1}), indicating a virtually identical C–O π-bond order in both compounds. In squaric acid, this π-bond order was calculated to be in the neighborhood of 0.8.[13] This requires a slight predominance of canonicals with α,β-diketone structure over those of the α,β-keto–enolate type. To reconcile this requirement with the approximate 60% iminium structure inferred from the ESCA data, we assign major importance in **3** to canonicals such as **3b**, in which negative charge is transferred from the N atoms to the benzene rings. On the other hand, the existing α,β-keto–enolate contribution must then for the most part be due to canonicals of the type **3c**, whereas forms with positive charge in the four-membered ring, such as **3d**, cannot be involved as major contributors. In order to compensate for the small (but certainly not negligible) contribution of **3a** and account for the excess iminium character over and above the 50% provided by forms such as **3b,c**, canonicals with unipositive charge on each nitrogen atom, exemplified by **3e**, are likely to be of major importance.

Table II
Thermogravimetric Analysis[a] of Polyamides 3, 4, and 3–4

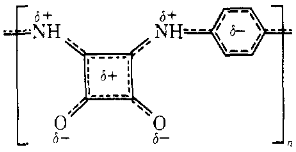
Polymer	Incipient wt loss temp range, °C	Rel residual wt, %[b]			
		600°	700°	800°	900°
3	325–375	74	71	69	67
4	375–425	76	74	72	71
3–4	350–400	75	71	68	66

[a] Under Ar; heating rate, 6° $\min^{-1}$. [b] Rounded to integral figures.

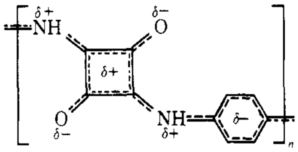
In **4**, available ir evidence[3] ($\nu_{CC,CO} \approx 1600$ cm^{-1}) points to a C–O π-bond order appreciably lower than found in **3**[14] and well in accord with a strong predominance of α,γ-keto–enolate forms, notably **4c**, and α,γ-diolate structures, such as **4d**.[15] The importance of **4d** is additionally emphasized by the need for accommodation of positive charge in the four-membered ring to compensate for the demonstrated inability of the N atoms to accept a higher positive charge than is concentrated on the N atoms of **3**. Furthermore, as in **3**, forms like **4e** with unipositive charge on each N atom[16] probably contribute strongly, compensating for ever so minor contributions by canonicals with uncharged N (**4a,b**) and accounting for the extra iminium character (50% provided by **4c,d**, etc.). The importance of form **4d** also derives from the electronic spectra. While the chromophore in **3**, resulting from such canonicals as **3b,c**, and **e**, most probably is carbonyl terminated, the chromophore in **4** almost certainly includes both amino groups of the recurring unit and, through form **e**, is capable of extending appreciably further along the chain, thus accounting for the more pronounced red shift in **4**. The intermediary $\lambda_{\max}$ value determined on polymer **3–4**, in which both unit types appear in random distribution along the chain, confirms this inference. The situation is quite analogous to that in the nonpolymeric compounds **1** and **2**, in which conjugation may optimally extend on the one hand (in **1**) over one anilino group and the attached enone or enolate system (**1b,c,d**), and on the other hand (in **2**) over both anilino groups and the interposed double bond (**2e**).[2]

As the greater extent of electronic delocalization in **4** should entail a higher stabilization energy[17] in this 1,3-interlinked polymer relative to the 1,2-interlinked isomer, one would expect **4** to exhibit a somewhat superior performance under conditions of the TGA test.[18] The tabulated data (Table II) confirm this expectation, although the difference is by no means significant. While both polymers exhibit quite excellent thermostability for polyamide structures, the relative weight loss in the two cases being in the vicinity of 30% at 800°,[19] thermal breakdown is distinctly delayed in **4** relative to **3**, and residual weights in the 700–900° region are higher by some 3–4%. Polymer **3–4**, as might be expected, undergoes incipient breakdown in a temperature range intermediary between **3** and **4**; residual weights in the 600–900° region practically coincide with those of the "weaker" polymer structure **3**.

In summary, we conclude from the spectroscopic findings that polyamides **3** and **4** both are distinctly mesoionic and hence should preferentially be represented by the delocalized (although not equivalent) structures shown:



3



4

Considerable positive charge, comparable in extent with that in the two nonpolymeric dianilides **1** and **2** and equivalent to about 60% iminium structure, is accumulated on the N atoms in both polymers. In **3**, negative charge is correspondingly transferred to the benzene rings and partially so to the carbonyl O atoms in agreement with a C–O π-bond order of about 0.8. In **4**, the extent of charge separation exceeds that in **3**; additional positive charge is likely to be delocalized on the four-membered ring, whereas additional negative charge is transferred to O according with a further reduced C–O bond order. The predominant iminium character in both polymers permits sufficient coplanar alignment of aromatic and four-membered rings to produce chromophores appreciably more extended than in **1** and **2**.

Experimental Section

Polyamides. Polymers **3**, **4**, and **3–4** were taken from the previous study.[3d] Their syntheses were accomplished, in the same order, by polycondensation of (i) squaryl dichloride and *p*-phenylenediamine in *N*-methylpyrrolidone (+2.5% LiCl)/pyridine (18:1 by volume) (expt 9); (ii) squaric acid and *p*-phenylenediamine in glycerol/pyridine (2:1 by volume) (expt 2); and (iii) squaric acid and *p*-phenylenediamine in polyphosphoric acid (expt 5 of that work[3d]).

Electronic Absorption Spectra. Spectra were scanned on KBr disks over the 300–550 nm region with a PYE Unicam SP 1800 ultraviolet spectrophotometer. The disks (thickness 0.25 nm; 0.005–0.015 mg of sample per 100 mg of KBr) were repeatedly pressed, crushed, ground, and repressed for minimization of background scattering.

X-Ray Photoelectron (ESCA) Spectra. AEI Scientific ES200 and Du Pont 650 electron spectrometers in the laboratories of respectively the Applied Physics Division, Bayer AG, Leverkusen, and the Instrument Products Division, Du Pont de Nemours & Co., Monrovia, Calif., were used for recording (ambient temperature, 10^{-6} Torr). The spectra were induced with Al Kα (1486.6 eV) radiation and were calibrated by reference against internal $NaNO_3$ and NH_4NO_3 (ES200; see text and Table I). An independent scanning series employed no internal standards; the spectra, induced with Mg Kα (1253.6 eV) radiation, were taken on a precalibrated instrument (Du Pont 650). Samples were applied in powder form onto gold-plated 6 × 13 mm probes.

Thermogravimetric Analysis (TGA). Thermograms were recorded on an Aminco thermoanalyzer in the U.S. Naval Ordnance Laboratory, Silver Spring, Maryland, at a heating rate of 6° min^{-1} in argon (flow rate, 28 l. hr^{-1}). As a precautionary measure, the samples were redried on the instrument for 30 min at 115–120° (no weight loss observed) prior to scanning. Residual weights were determined by reference to a base line established in a blank run employing empty crucible.

Acknowledgment. This investigation was supported by the Council for Scientific and Industrial Research and the Atomic Energy Board. The cooperation of Dr. H. J. Booth, U.S. Naval Ordnance Laboratory, in obtaining the TGA thermograms, and of Dr. M. Czuha, Jr., Du Pont Instrument Products Division, in recording the ESCA spectra on the Du Pont 650 electron spectrometer, is gratefully acknowledged. B. R. G. thanks the National Institute for Metallurgy for a scholarship grant.

References and Notes

(1) (a) University of the Witwatersrand; (b) Bayer AG.

(2) E. W. Neuse and B. R. Green, *J. Am. Chem. Soc.*, **97**, 3987 (1975).

(3) (a) J. Gauger and G. Manecke, *Int. Symp. Macromol. Chem., Prepr., 1969*, **1**, 31 (1969); *Angew. Chem., Int. Ed., Engl.*, **8**, 898 (1969); (b) G. Manecke and J. Gauger, *Makromol. Chem.*, **125**, 231 (1969); (c) B. R. Green and E. W. Neuse, *Polymer*, **14**, 230 (1973); (d) E. W. Neuse and B. R. Green, *Polymer*, **15**, 339 (1974).

(4) (a) The chemistry of 1,2- and 1,3-disubstituted derivatives of squaric acid has been proficiently reviewed;[4b–d] (b) G. Maahs and P. Hegenberg, *Angew. Chem., Int. Ed. Engl.*, **5**, 888 (1966); (c) H.-E. Sprenger and W. Ziegenbein, *ibid.*, **7**, 530 (1968); (d) W. Ried and A. H. Schmidt, *ibid.*, **11**, 997 (1972).

(5) The limitations of the representation **4a** with dipositive four-membered ring center were emphasized in our previous investigation.[3d]

(6) Although neither synthesis leads to products exclusively of either the 1,2- or the 1,3-disubstituted types, we accept the two polymers as being representative of the two limiting structural types, since the populations of "contaminating" 1,3-disubstituted units in **3**, and likewise those of 1,2-disubstituted units in **4**, are low enough to be neglected for the present purpose.

(7) G. R. Griffiths, M. D. Rowe, and G. A. Webb, *J. Mol. Struct.*, **8**, 363 (1971).

(8) Once separated and dried, poly(squarylamides) of higher molecular mass are not dissolved by nonacidic media. In strong protonic acids, such as H_2SO_4, both **3** and **4** (as well as intermediary structures, e.g., **3–4**), while dissolving readily, are protonated in this process. Protonation occurs on oxygen as reflected in strong bathochromic effects (stabilization of enolate forms possessing long chromophores); N protonation, in contrast, would enhance sp^3 hybridization on that hetero atom, effectively reducing the lengths of the chromophores to those in **5** and **6**.

(9) (a) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1968); (b) J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968); (c) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

(10) Although the accuracy is very poor (estimate ±0.13), we are interested here only in relative values and, hence, are concerned with the precision of our experiments, which, as in the preceding work,[2] is ±0.04.

(11) Percentage arrived at by interpolation of $q_{N(3)}$ between $q_{N(3a)}$ and $q_{N(3e)}$, and of $q_{N(4)}$ between $q_{N(4b)}$ and $q_{N(4e)}$. Nitrogen atom charge parameters for limiting canonicals calculated by the Pauling–Siegbahn method.[9a]

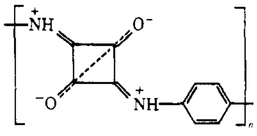
(12) The algebraic mean is used here instead of the more accurate root mean square. For a justification of this approach, see footnote 6a in ref 2.

(13) S. Skujins and G. A. Webb, *Spectrochim. Acta., Part A*, *25*, 917 (1969). These authors calculated values of 0.715 and 0.862, respectively, by HMO and Pariser–Parr–Pople methods.

(14) We find qualitative confirmation of this trend in the O(1s) ESCA spectra, lower binding energies (corresponding to more negatively charged nuclei) being found in **2** (530.7 eV) and **4** (530.5 eV) than in the corresponding species **1** (531.0 eV) and **3** (530.9 eV). However, the O(1s) peak resolution is too low (line width at half-height, 3.2 ± 0.4 eV) to allow for a quantitative evaluation. The same holds for the C(1s) peaks, found too broad and poorly resolved for an assessment of carbon atom charges.

(15) As was pointed out above, forms **4a** and **4b**, although qualifying here on grounds of ir evidence, must be disregarded as major contributors for lack of participation of the amino groups in the chromophores.

(16) (a) This category includes the canonical shown, implying electronic 2,4-cross-ring interaction. Although less probable than **4e**, this form, supporting the p_{C-O} derived from ir data, finds theoretical justification in HMO calculations[16b] of the electronic systems of similar structures, which indicate such cross-ring interaction to provide additional stabilization by some 0.3–0.8β. (b) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 1793 (1960).



(17) The expectation of superior stabilization in **4** can also be derived from the greater numbers of set-wise degenerate canonicals in **4** than in **3**. There are, for example, four equivalent (and hence isoenergetic) representations each of **4c** and **4e** as against two such representations of the corresponding forms **3c** and **3e**; furthermore, **4d**, with four isoenergetic representations, has no important counterpart in **3** and so more than offsets the major weight of **3b** in the 1,2-linked polymer.

(18) The thermo-oxidative stability of **4** was investigated[3b] under isother-

mal conditions (2 hr at 350°), but no isomer comparison is possible here, as 3 was not included in that work.

(19) (a) For comparison, all-aromatic (1,3- and 1,4-phenylene linked) polyamides, while exhibiting a higher temperature range of incipient breakdown (430–470°), gave relative residual weights of about 50–65% at 600° and 45–60% at 700° (15° min^{-1}; N_2).[19b,c] (b) J. Preston, *J. Polym. Sci., Part A-1*, **4**, 529 (1966). (c) F. Dobinson and J. Preston, *ibid.*, **4**, 2093 (1966).

A Study of Molecular Motion in Polymeric Solids by Electron–Electron Double Resonance

M. M. Dorio and James C. W. Chien*

Department of Chemistry, Polymer Research Institute and Materials Research Laboratories, University of Massachusetts, Amherst, Massachusetts 01002. *Received June 4, 1975*

ABSTRACT: Single-line ELDOR (electron–electron double resonance) has been used to study molecular motion in polymeric solids. Saturating one spin-packet in an inhomogeneous hyperfine envelope and observing another spin-packet within the same envelope provides a means to determine molecular reorientation as saturation transfer deenhances the ESR transition probability. The ELDOR reduction factor was found to increase with the decrease of temperature in a $1/T$ dependence for different nitroxides dissolved in polystyrene and polypropylene. There is no observable difference between the amorphous and semicrystalline polymers. The nitroxides are mainly in the amorphous phase and its motion is not affected by the presence of the crystalline phase. Polystyrenes spin-labeled on the terminal and side-chain phenyl groups were studied and were found to differ in ELDOR response. The motions of nitroxides in a given polymer are greater for the small-size di-*tert*-butyl nitroxide and smallest for the large maleimide nitroxide. There is also observed a matrix ELDOR signal at the free proton frequency of 13.5 MHz. It is observed only below T_g and in both amorphous and semicrystalline polymers. This may suggest a local order in a polymer solid. Matrix signals in monomer solids are only seen in the polycrystalline state but vanish in the glassy state.

The physico-mechanical properties of a solid polymer are dependent on the molecular motions. Several methods are useful in the study of these motions, such as dielectric relaxation, dynamic mechanical relaxation,[1] and wide-line NMR.[2] The purpose of this paper is to introduce a new technique electron–electron double resonance, ELDOR, which complements the others as well as offering some unique features.

Of course electron spin resonance, ESR, has been used quite extensively to probe molecular motion. The method has seen applications in biological systems[3] and in polymers.[4-11] All these studies[4-11] were made either on polymer solutions or on polymers in the vicinity and above their melting points. Such is the limitation of the EPR method because line width changes are measurable only for motions with $5 \times 10^{-9} \leq \tau_c \leq 10^{-7}$ sec which is the order of the magnetic anisotrophy. Beyond the short τ_c limit, where τ_c is the rotational correlation time, the line width is determined by unresolved hyperfine splittings. Above the long τ_c limit, powder ESR spectra were obtained.

ELDOR effects for free radicals in solution were first reported by Hyde, Chien, and Freed.[12] This and many subsequent studies explored the effect of saturating one ESR transition on another transition being observed with low microwave power. Since these transitions do not share any common energy level, the transfer of saturation depends upon relaxation processes. An intramolecular electron–nuclear dipolar (END) process and an intermolecular Heisenberg exchange process were found to be responsible for much of the ELDOR effect. Theories have been developed[12,13] to describe these.

Recently, the works of Dalton and coworkers[14] and in our laboratories[15] showed that the ELDOR spectra appear sensitive to τ_c as long as 10^{-3} sec. Therefore, ELDOR can be used to study molecular motions over seven orders of magnitude. In these studies emphasis was placed on single-line ELDOR where the pump and observing frequencies are both set within a single inhomogeneous ESR envelope.

The extension of ELDOR into the long τ_c region suggests the possibility of studying molecular motions in bulk polymers. The central purpose of this work is to apply ELDOR to the study of two types of motion in polymeric materials: those of the macromolecules and those of low molecular weight additives. Results on polystyrene with nitroxide labels either on the terminal groups or on the side chain phenyl rings are described. Also presented are the results of various nitroxide molecules added interstitially to polypropylene and polystyrene.

Experimental Section

Three nitroxides were used in the interstitial experiments. The 4-*N*-maleimido-2,2,6,6-tetramethylpiperidine-1-oxyl (maleimide) was synthesized according to the procedure of Griffith and McConnell.[16] 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL) was obtained from Synvar and di-*tert*-butyl nitroxide (DTBN) from Eastman Organics.

Amorphous polypropylene was Easbond from Tennessee Eastment Co.; semicrystalline polypropylene, Profax 6501, is the product of Hercules, Inc. Amorphous and semicrystalline polystyrene were from Monsanto and Dow Chemical Co., respectively.

To incorporate nitroxides into polystyrene and amorphous polypropylene, the polymer was dissolved in spectral grade benzene (Baker) and nitroxide was added. The solution was dropped onto Teflon sheets and the solvent was removed under vacuum to constant weight. In the case of semicrystalline polypropylene, it was swollen with a benzene solution of nitroxide for several days. The polymer was filtered and washed with benzene and vacuum dried to constant weight. The concentration of the additive was always less than 0.2% by weight which is $<10^{-3}$ *M*; it is found only in the amorphous phase.

Two different types of spin-labeled amorphous polystyrene were used in these experiments. One was labeled at the para position of the phenyl group (SL 1).