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Electron Spin Resonance Study of Radicals in Photopolymerized Di(meth)acrylate Network

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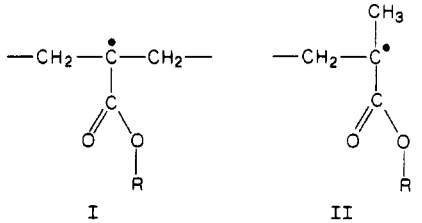
ABSTRACT: ESR spectra of free radicals trapped in photopolymerized HDDA (1,6-hexanediol diacrylate) and HDDMA (1,6-hexanediol dimethacrylate) were (re)examined. Careful analyses of the spectral patterns, the hyperfine structures due to β-protons, revealed that the radicals in the polymethacrylate are the propagation radicals of the conformation with the least strain energy (trans form) and those in the polyacrylate are the midchain radicals resulting from the C_α–H_α cleavage at diad sectors of the conformation with the highest strain energy (gauche–gauche form). When both polymers were formed on an inert high-surface-area substrate and exposed to oxygen at low temperature (−18 °C), instant conversion of the radicals to the peroxy radicals ROO• was observed. The resulting peroxy radicals decayed rapidly at room temperature ($t_{1/2}$ = ~3 min).

Introduction

A densely cross-linked poly(meth)acrylate network produced by polymerization of multi(meth)acrylate (e.g., 1,6-hexanediol diacrylate) is used in many commercial applications.[1] The monomer formulation typically contains several weight percent of radical photoinitiator such as α,α-dimethoxy-α-phenylacetophenone and is *photopolymerized* by exposure to UV light. It is not surprising that the dense polymer network thus created hosts either the propagation radical or the secondary radical product of the polymerization processes trapped as the monomer ingredients are consumed, and the rigidity and size of the polymer network increase rapidly during the photocuring process.

Kloosterboer et al. indeed reported on the ESR spectra of stable radicals trapped in photopolymerized 1,6-hexanediol diacrylate (HDDA)[2] and bis(2-hydroxyethyl)bisphenol A dimethacrylate (HEBDMA).[3] The stable radical in the former network was identified unequivocally, through the use of HDDA deuterated in the α position of the acrylate sector, as the midchain radical I resulting from



I II

the C–H cleavage at the α position of the acrylate chain.[2] The stable radical in the latter network exhibited the well-known, well-characterized "5 + 4" line ESR pattern ascribed to the propagation radical II of the methacrylate chain.[4]

The ESR spectrum of the midchain radical observed from polymerized HDDA (I) has an appearance of being a 1:2:1 triplet of ~25-G spacings. The pattern was hence attributed to the hyperfine (hf) interaction of ~25 G with one proton each of the two β-methylene groups and negligibly small hf interaction with the remaining β-protons.[2] The reported spectrum of the midchain radical, however, does not possess a simple 1:2:1 triplet pattern. A further scrutiny of the spectrum appeared warranted; a successful scrutiny should shed light on the conformation of radical sites. The "5 + 4" line pattern of the propagation radical II of the polymethacrylate system had long eluded a definitive assignment but was elegantly elucidated by Iwasaki and Sakai as that arising from the hf interactions of the protons of a freely rotating methyl group and those of the β-methylene group in a certain conformation with some statistical scatter.[5]

Kloosterboer et al. also reported that the radicals I and II trapped in the network of polymerized HDDA and HEBDMA were extremely stable under vacuum at room temperature but decayed rapidly at room temperature under oxygen. No ESR signal due to peroxy radical was detected, however.[2]

The present paper reports on the results of detailed analysis of the ESR spectra of the midchain and propagation radicals I and II detected in photopolymerized HDDA and HDDMA (1,6-hexanediol dimethacrylate). The analysis revealed that the midchain radical I was generated at sites where the diad segment of the acrylate chain had the conformation of the highest strain energy (gauche–gauche form), while the conformation of the propagation radical II was consistent with the methacrylate chain end having the conformation of the least strain energy (trans form). We also succeeded in observing (by ESR) instant conversion of radicals I and II to peroxy radicals on exposure to oxygen. It was achieved by dispersing the monomer formulations on an inert, high-surface-area substrate (porous Vycor quartz). The resulting peroxy radicals decayed rapidly at room temperature.

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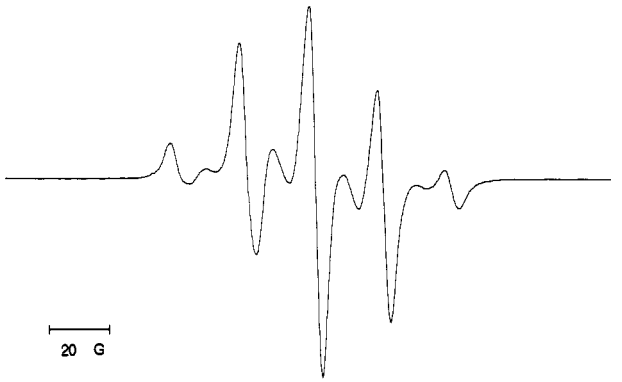


Figure 1. ESR spectrum of photocured HDDMA.

Experimental Section

For the present series of experiments the monomer formulations were prepared by adding and thoroughly mixing 4 wt % of DMPA (α,α-dimethoxy-α-phenylacetophenone from Aldrich Chemical) with HDDA (1,6-hexanediol diacrylate from Aldrich Chemical) and HDDMA (1,6-hexanediol dimethacrylate from Sartomer Co.). For sake of brevity these formulations will be called HDDA and HDDMA, respectively, in the following sections.

Samples for observation of the ESR spectra of the midchain and propagation radicals I and II were prepared as follows: 2-mm-o.d. quartz rods were dipped into the respective monomer formulations, exposed to UV light (an Oriel 1-kW mercury–xenon lamp equipped with a Corning 7-54 UV filter) for 60 s, then placed in quartz tubes (4-mm o.d., 3-mm i.d.), evacuated (below 1 μm Hg), and sealed at room temperature.

Samples supported on high-surface-area material were prepared by immersing porous Vycor quartz powder (Corning Product 7930) in the monomer formulations, letting them stand overnight, and then vacuum filtering the material with several washings with acetone until the powder appeared dry. The powders thus treated were placed in quartz tubes, evacuated, and sealed.

ESR spectra were obtained by using an ER100D (IBM Instruments) X-band spectrometer. Unless stated otherwise the spectra discussed below were all obtained at room temperature, and the spectrometer frequency locked to the sample cavity was 9.26 GHz.

ESR Spectra and Assignments

It is pertinent to note that for both the midchain radical I and the propagation radical II there are no α-protons and the prominent hyperfine structures are caused only by the β-protons. It has been well established that for an alkyl radical in which the unpaired electron resides in the p_π orbital of an sp^2 hybridized α-carbon, the hf coupling constant of a β-proton depends on the dihedral angle of the C_β–H_β bond relative to the p_π orbital as follows:[6]

$$A(H_\beta) = B_0 + B\cos^2\theta \cong B\cos^2\theta \qquad (1)$$

Here θ is the dihedral angle (that between the projections of the p_π orbital and the C_β–H_β bond upon the plane perpendicular to the C_α–C_β bond). The second equation holds as B_0 is small ($\sim$2 G) compared to B ($\sim$50 G). For a freely rotating methyl group at the β position, $\langle\cos^2\theta\rangle = {}^1/_2$; thus expected is a 1:3:3:1 quartet with the successive spacings of $\sim$25 G.

Figure 1 shows the ESR spectrum observed from our photocured HDDMA. As in the case of HEBDMA reported earlier,[3] the spectrum of photocured HDDMA is identical with those observed from various methacrylate systems and assigned to the propagation radical II. The g value determined from the spectrum observed here is 2.0028 (6). As stated earlier, Iwasaki and Sakai[5] demonstrated that the spectrum of the propagation radical II could be accounted for by the β-proton hf interactions of a rapidly rotating methyl group and the adjacent methylene group having a conformation slightly offset from a symmetric arrangement where the two protons would both have dihedral angle of 60°. The situation is depicted in Figure 2.

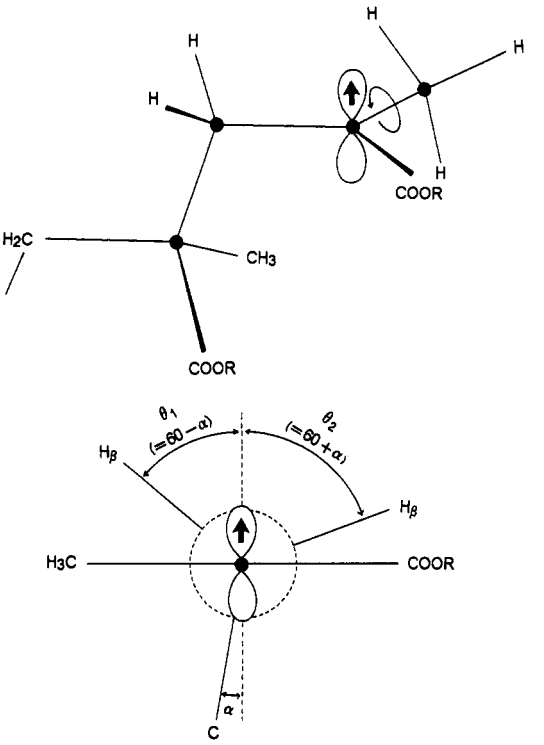


Figure 2. Propagation radical of polymethacrylate chain and its Newman diagram.

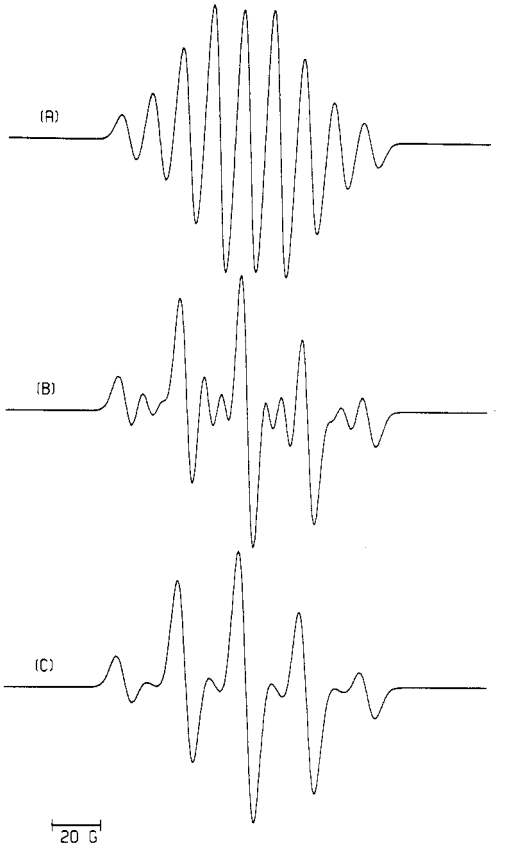


Figure 3. Simulated ESR spectra of the propagation radicals of polymethacrylate chain. The spectra were computed assuming (A) $\theta_1 = \theta_2 = 60°$, (B) a tilt angle α of 5° for the β-methylene group, and (C) tilt angles with a Gaussian scatter of $\Delta\alpha_{1/2} = \pm 8°$ centered about the most probable tilt angle $\alpha_0 = 5°$.

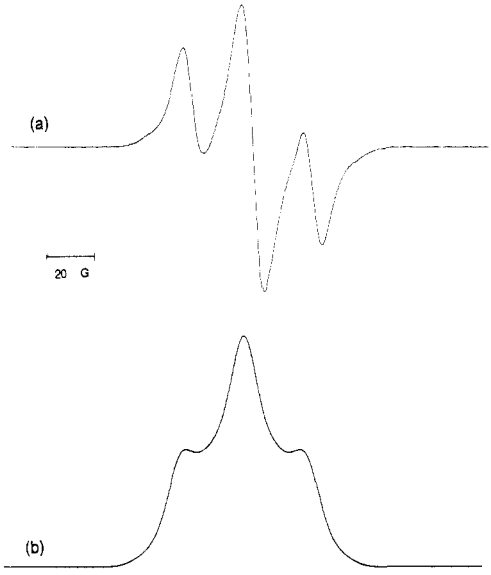


Figure 4. (a) ESR spectrum of photocured HDDA and (b) its integral.

Figure 3A is a computer-simulated spectrum of the propagation radical II assuming a hf coupling constant of 25 G for a freely rotating methyl group and the hf coupling constants of the methylene protons given by eq 1 for $\theta_1 = \theta_2 = 60°$. For the simulation a Gaussian line shape with the full width at half-height of 8 G was assumed for *individual* components. Figure 3B is a spectrum of the same radical computed assuming a tilt angle $\alpha = 5°$ of the methylene group from the symmetric position (hence $\theta_1 = 55°$ and $\theta_2 = 65°$). Figure 3C shows the computed spectrum obtained when a Gaussian distribution with $\Delta\alpha_{1/2} = \pm 8°$ is assumed for the tilt angle centered about the most probable value $\alpha_0 = 5°$. These spectra are basically reproductions of those reported earlier by Iwasaki and Sakai.[5,7] They are presented here to facilitate the comparison and add credence to the analysis of the spectrum of the midchain radical presented next.

Figure 4a shows the ESR spectrum observed from our photocured HDDA. It is identical with that reported earlier.[2] The g value of the spectrum was measured to be 2.0028 (6). The observed derivative pattern is shown integrated in Figure 4b. It is apparent that the ostensive triplet is not a simple 1:2:1 triplet due to hf interactions with two equivalent protons.

The genesis of the midchain radical I must be the hydrogen abstraction from the α-carbon of the *already formed polyacrylate network* by the propagation and/or other reactive radicals during the photocuring process. After the C_α–H_α cleavage the spatial displacements needed in the region in order to attain and accommodate the sp^2 hybridization of the α-carbon are rather small (Figure 5). It follows that the conformations of the two β-methylene groups flanking the radical site must reflect the conformation of that sector of the polyacrylate chain prior to the C_α–H_α cleavage.

Three possible conformations (trans, gauche, and gauche) of a methylene group relative to an adjacent C_α group in a polyacrylate chain are shown in Figure 6. It is apparent that both the trans and gauche conformations lead to the dihedral angles of 0° and 60° for the β-methylene protons of the resulting radical, and the gauche form leads to the symmetric arrangement of $\theta_1 = \theta_2 = 60°$. Thus for the midchain radical I of polyacrylate network there are only three possible arrangements of the two β-methylene groups as given by the dihedral angles of the C_β–H_β bonds, i.e., (0,60; 0,60), (0,60; 60,60), and (60,60; 60,60). The actual dihedral angles may not be exactly at these values but are surely within their proximities (±15°).[8]

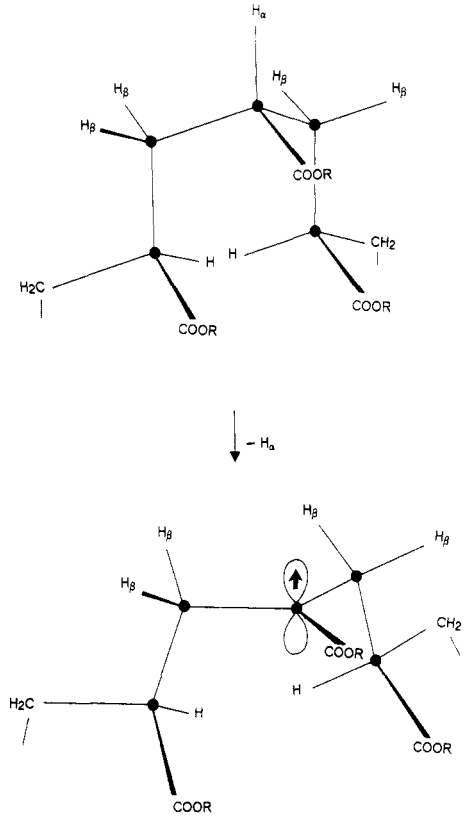


Figure 5. Schematic depiction of a diad sector of a polyacrylate chain before and after the C_α–H_α bond cleavage. A diad section with the gauche–gauche conformation is shown.

Figure 7, parts A–C, shows, respectively, the spectra of the midchain radical I computed for the three conformations. The spectrum of the conformation (0,60; 0,60) (Figure 7A) and that of the conformation (0,60; 60,60) (Figure 7B) have overall spreads of ~120 and ~90 G, respectively. These values altered little when the tilt angle of up to ±15° was allowed for each methylene group. They are clearly much larger than the overall spread of the observed spectrum (~60 G, Figure 4a). The overall spread of the spectrum of the conformation (60,60; 60,60) (Figure 7C) is ~60 G. Figure 8 shows how this spectrum changed when the tilt angle α of 10° was assumed for the two methylene groups, and subsequently tilt angles with a Gaussian scatter of $\Delta\alpha_{1/2} = \pm 10°$ were assumed centered about the most probable value $\alpha_0 = 10°$. The agreement between the observed and simulated spectra (Figures 4a and 8C) is gratifying. In the computation of the last spectrum the Gaussian scatters of the two methylene groups were assumed to be independent from each other. A much poorer agreement resulted when the two methylene groups were assumed to be *locked* (the outer components of the triplet appeared ca. one-half as intense as seen in Figure 8C).

Comparison of Figures 4a and 8C reveals that in the observed spectrum of midchain radical I there are additional shoulders outside the outer components of the main triplet. It was realized that the adiditional signal might be ascribed to the midchain radical of the conformation (0,60; 60,60). Figure 9 shows the spectrum of the midchain radical I computed for the conformational mixture of 86% (60,60; 60,60) and 14% (0,60; 60,60). Again, for all the methylene groups in both conformations, tilt angles with a Gaussian scatter of $\Delta\alpha_{1/2} = \pm 10°$ centered about the

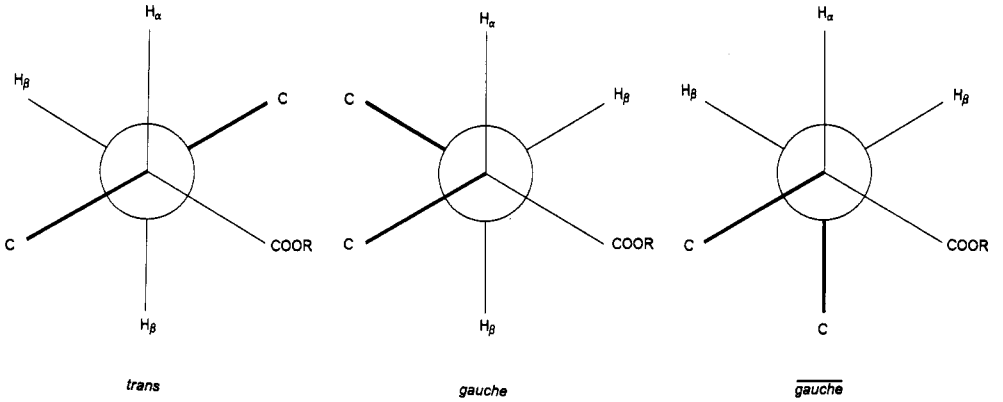


Figure 6. Newman diagrams showing three possible conformations of an acrylate unit in a polyacrylate chain. The heavy lines indicate the bonds in the skeletal chain.

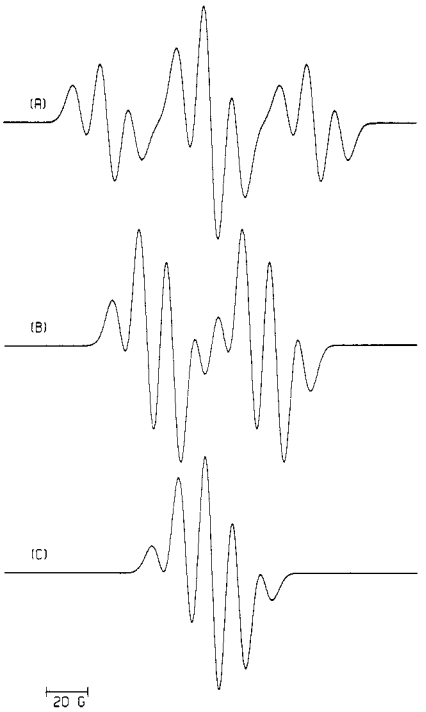


Figure 7. Simulated ESR spectra of the midchain radicals of polyacrylate. The spectra were computed assuming the dihedral angles of (a) (0,60; 0,60), (b) (0,60; 60,60), and (c) (60,60; 60,60) degrees for the protons in the two β-methylene groups.

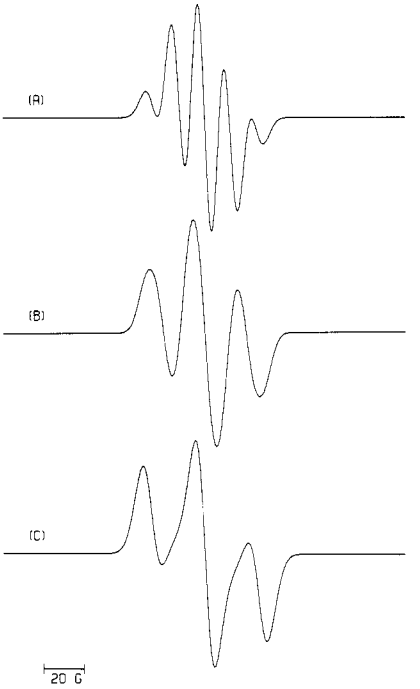


Figure 8. Simulated ESR spectra of the midchain radicals of polyacrylate of gauche–gauche conformation: (A) the β-methylene groups are both in the perfectly staggered gauche position, (B) a tilt angle of 10° from the symmetric position is assumed for the β-methylene groups, and (C) tilt angles with a Gaussian scatter of $\Delta\alpha_{1/2} = \pm 10°$ centered about the most probable tilt angle $\alpha_0 = 10°$ are assumed for the β-methylene groups.

most probable value $\alpha_0 = 10°$ were assumed. The shoulders appeared slightly more intense for samples irradiated at low temperature (0 °C) and for samples prepared on porous Vycor quartz (vide infra).

Reaction with Oxygen

Decay rates of the midchain radical I trapped in photocured HDDA and that of the propagation radical II trapped in photocured HDDMA were measured at room temperature (Figure 10). In one series the samples were kept sealed in vacuum, and in the other the samples tubes were left open to ambient atmosphere. The rapid decay of the signals observed for samples exposed to air must be due to reaction with oxygen. ESR signals due to the expected peroxy radical, ROO•, were not observed from these samples, however. The decay rate of the peroxy radical must be faster than its production rate, the latter being determined by the diffusion rate of oxygen.

To realize a faster conversion of the primary radicals to the peroxy radicals on exposure to oxygen, the monomer formulations were dispersed on inert, high-surface-area substrate (porous Vycor quartz), evacuated and sealed in quartz tubes, and then exposed to UV light at room temperature. The resulting materials showed the expected ESR spectra of the midchain radical I and the propagation radical II, respectively (Figures 11a and 12a). It is interesting that the spectrum of HDDA here (Figure 11a) shows noticeably more intense shoulders due to the midchain radical of the conformation (0,60; 60,60).

These samples were then cooled to −18 °C, exposed to air (for several seconds), evacuated and sealed at −18 °C, and quenched to 77 K. Figures 11b and 12b show the ESR spectra observed at 77 K of the samples thus treated. Other than the weak signals at the high-field end due to remnant original radicals, the two spectra are now identical. They are characterized by an orthorhombic **g** tensor of $g_1 = 2.034$, $g_2 = 2.008$, and, $g_3 = 2.002$. The **g** tensor is that typically expected for the peroxy radical, ROO•.[9] When warmed to room temperature, the peroxy radicals decayed rapidly with $t_{1/2} = \sim 3$ min. Only a partial conversion to the peroxy radical was achieved when the samples were exposed to air at −78 °C, and very little conversion at 77 K.

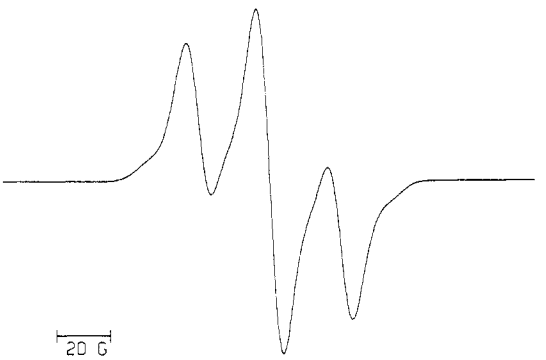


Figure 9. ESR spectrum of the midchain radicals simulated for a conformational mixture of 84% (60,60; 60,60) and 16% (0,60; 60,60) conformers. Tilt angles α with a Gaussian scatter of $\Delta\alpha_{1/2} = 10°$ centered about the most probable tilt angle $\alpha_0 = 10°$ were assumed for all the β-methylene groups.

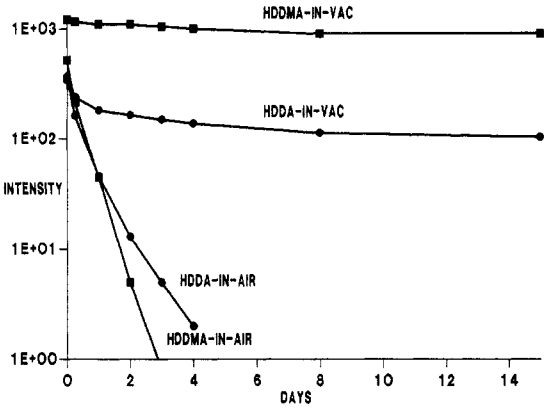


Figure 10. Decay at room temperature of the propagation radicals trapped in photocured HDDMA and the midchain radicals trapped in photocured HDDA.

Discussion

The most probable tilt angle for the β-methylene group in the propagation radical trapped in photocured HDDMA is thus determined as 5°. Equation 1 then gives 16 (1) and 9 (1) G as the most probable hf coupling constants of the β-protons. For the two conformers of the midchain radicals found in photocured HDDA, the most probable hf coupling constants similarly determined are for the major conformer (60,60; 60,60) 21 (1) and 6 (1) G for the two protons in each methylene group, and for the minor conformer (0,60; 60,60) 49 (1) and 6 (1) G for the protons in the first methylene group, and 21 (1) and 6 (1) G for the protons in the second methylene group.

Conformational characteristics of poly(methyl acrylate) and poly(methyl methacrylate) have been examined extensively.[10-13] The conformation of the skeletal chains of these polymers is determined by the intrinsic 3-fold torsional potentials about the skeletal C–C bonds and the interactions between nonbonded atoms and/or groups in the side chains. As depicted in Figure 6, the conformation of an individual acrylate unit in the chain is thus classified as either trans, gauche, or gauche depending upon the relative positions of the skeletal bonds in the Newman diagrams. It is readily seen that, for a single acrylate unit in the chain, the trans conformation has the least steric hindrance between the nonbonded groups, and the gauche conformation has the most.[10]

Being at the propagating end of a chain, the propagation radical II should have little difficulty in attaining the conformation of the least strain energy. The Newman diagram at the α-position of the propagation radical depicted in Figure 2 shows that the observed conformation is indeed that with the least steric hindrance and that conducive to render the trans–trans diad arrangement to the growing chain.

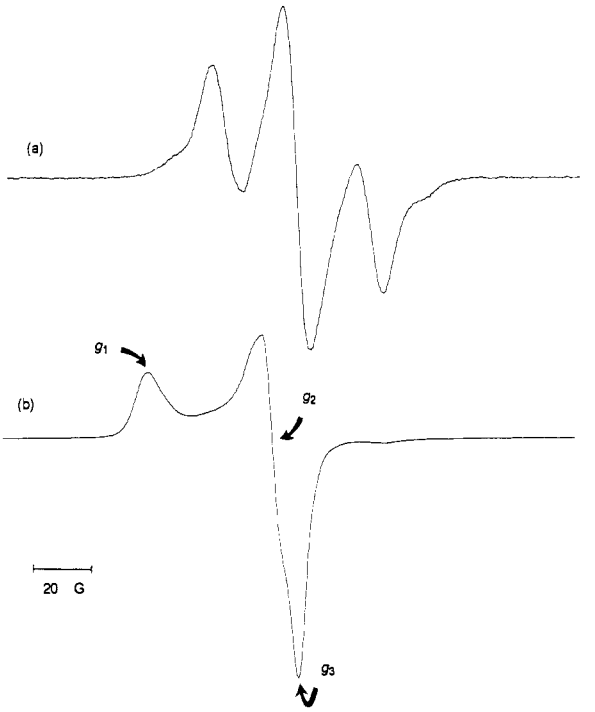


Figure 11. ESR spectra of HDDA dispersed on porous Vycor quartz: (a) observed at room temperature after a fresh sample had been exposed to UV light at room temperature; (b) observed at 77 K after the sample in (a) was subsequently cooled to −18 °C, exposed to oxygen, evacuated, and then quenched to 77 K.

The present study revealed that the majority of the midchain radicals in photocured HDDA originated from diad sectors of the gauche–gauche conformation. According to the analysis by Flory et al. the gauche–gauche diad in the poly(methyl methacrylate) chain has the highest strain energy and is at least 35 kcal mol^{-1} above the most stable trans–trans diad conformer.[10] Figure 5 depicts a gauche–gauche diad conformer in a poly(methyl acrylate) chain. It clearly illustrates the severe steric hindrance between the ester groups in the adjoining acrylate units. The figure also illustrates how exposed (and hence vulnerable to a radical attack) the α-hydrogen of this diad is and how the strain energy of the sector may be mitigated by the sp^2 rehybridization of the α-carbon upon the C_α–H_α bond cleavage. The formation of the midchain radicals at the gauche–gauche diad sectors is thus favored by a thermodynamic factor and a kinetic factor as well.

In the methacrylate system undergoing polymerization process, the propagation radical is a tertiary radical. In the acrylate system similarly undergoing polymerization process, the propagation radical is a secondary radical, while the midchain radical I is a tertiary radical. The dominance of the propagation radical II in photocured HDDMA and that of the midchain radical I in photocured HDDA are thus ascribed to the thermodynamic stability of the tertiary radicals over the secondary radicals.

It is not unexpected that when (meth)acrylate polymers already formed are subjected to ionizing radiations at low temperature, many other radicals are generated. Geuskens and David γ-irradiated poly(methyl acrylate) at liquid nitrogen temperature and examined the evolution of the ESR spectra as a function of temperature.[14] A similar study was carried out for poly(ethyl acrylate) by Hesse et

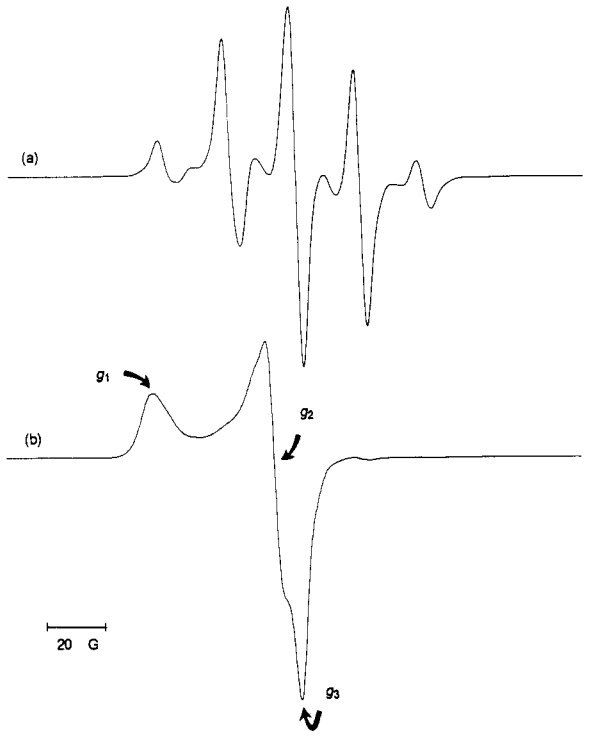
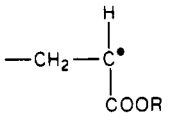


Figure 12. ESR spectra of HDDMA dispersed on porous Vycor quartz: (a) observed at room temperature after a fresh sample had been exposed to UV light at room temperature; (b) observed at 77 K after the sample in (a) was subsequently cooled to −18 °C, exposed to oxygen, evacuated, and then quenched to 77 K.

al.[15] Both studies reported that the ESR spectrum due to initially formed radicals evolved and decayed on warming, and at or near room temperature the spectrum became *a triplet with splitting of 25 G*. The final spectrum had been assigned to



The final triplet pattern reported in either study appears identical with that seen in Figure 4a. It is most likely that the final triplet observed in the γ-radiation studies are also due to the midchain radicals formed as the result of radical attack on the gauche–gauche diad sectors of acrylate chains.

Registry No. HDDA, 57592-67-3; HDDMA, 27813-91-8.

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(6) See, for example, ref 4, p 129.
(7) In the present study B in eq 1 was assumed to be 50 G, hence the proton coupling constant of 25 G for the rotating methyl group as compared to B = 46 G in ref 5.
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