Chemistry of Polymerization Products of p-Benzoquinone. ^{13}C NMR and Molecular Dynamics Study

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ABSTRACT: Proton and carbon-13 nuclear magnetic resonance as well as energy minimization and molecular dynamics calculations were all used to study chemical structures and single chain contributions of non-oxidized, completely oxidized and completely reduced polymerization products of p-benzoquinone. Polyquinones are shown using NMR techniques to have been transformed into polybenzoquinone upon oxidation. The negatively charged oxygen atoms of the polybenzoquinone are thus responsible for the increased torsion of the benzoquinone nuclei about connecting bonds. This should lead to lesser energetic dynamics with respect to the bending of its nuclei. Polyhydroquinone are completely stabilized by the presence of the hydrogen bonding not available to polybenzoquinone. Nuclei bending in this case is greatly influenced by the more restricted torsion behavior. Polyquinones, a mixture of both, shows inbetween behavior but more on the polyhydroquinone side which indicates the greater presence of the hydroquinone nuclei in an equimolar ratio compound.
    KEY WORDS   Benzoquinone / Polymerization / Nuclear Magnetic Resonance / Molecular Mechanics / Energy Minimization / Molecular Dynamics /

The incorporation of polymerization products of p-benzoquinone into a sulfur cured rubber matrix such as styrene–butadiene rubber (SBR) has profound effect on the mechanical properties of the elastomeric networks.[1,2] The ability of these materials to bind chemically to the sulfur cured rubbery chains through the radical sites created during slow degradation has resulted into the formation of networks with bimodal chain length distribution.[3] The superior mechanical properties observed for these networks were due to the presence of the elastically effective long polyquinone chains assumed to contribute to the modulus of the samples by increasing their end-to-end distances and decreasing their entropies in response to the imposed stress.[4]

The better mechanical properties of the networks were also attributed to the ability of these polymers to act as radical traps in blocking the radical sites created on the rubbery chains during the degradation, thus forming the mechanically anomalous bimodal networks. The capacity of these polymers in protecting the elastomeric networks and improving their mechanical properties thus depends a great deal on the quinonoid/benzenoid ratio results as a consequence of the polymerization process of p-benzoquinone.[5] Hydroquinone units (benzenoid nuclei) and benzoquinone units (quinonoid nuclei) comprising the polyquinone chains (AQ), Figure 1a, are well known for their effectiveness as inhibitors for the radical polymerization of various monomers[6] and so they are expected to participate in radical chain degradation.

Naturally, polyquinones are susceptible to reduction and oxidation.[5] Reduction of these materials transforms the quinonoid nuclei into benzenoid ones with loss of conjugation, thus producing a colorless material. The unstable reduced material, polyhydroquinone (HQ), Figure 1b, is easily reoxidized on exposure to air, reforming the original brown product. A certain equilibrium within the single polyquinone chains between the hydroquinone and benzoquinone forms seems to be

maintained through intramolecular and intermolecular hydrogen bonding. The oxidized form of polyquinone, polybenzoquinone (BQ), Figure 1c, could be obtained as well through the mild oxidation using iodine solution in tetrahydrofuran (THF) with an increased quinonoid/benzenoid ratio. Strong oxidizing systems such as permanganate solution in acetone has led to complete loss of the quinonoid nature of the polymers. Interest in the quinonoid/benzenoid ratio of polyquinone has developed since the realization that oxidized polyquinones have a better effect in protecting and improving the quality of elastomeric networks. This is especially when
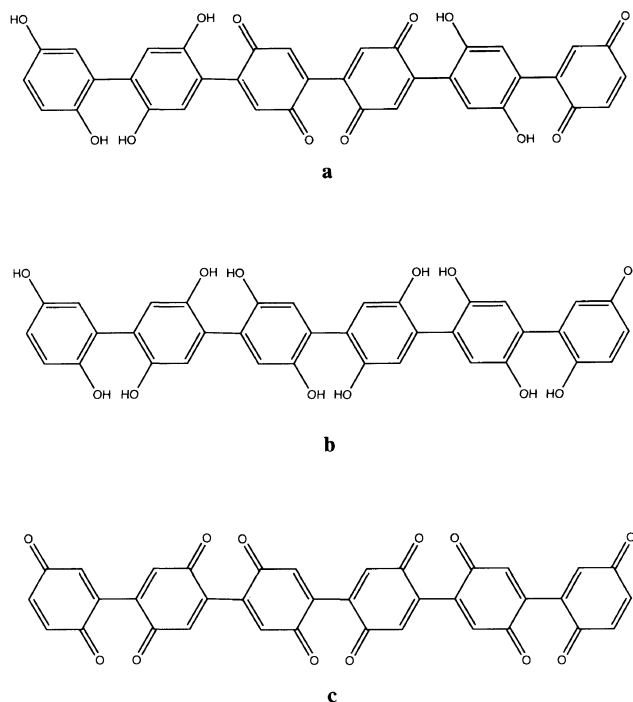
Figure 1. Sketches of the three products resulting from the polymerization of p-benzoquinone. The top structure, a, corresponds to polyquinone. The second one, b, to polyhydroquinone and the third one, c, to polybenzoquinone. In this figure and the simultaneous ones this sequence of identification is respectfully followed.

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coupling polyquinones with commercially available anti-oxidants.[1-3]

Since on the incorporation of the polymerization products of p-benzoquinone into the sulfur cured rubber matrix, a network with bimodal chain length distribution is produced, then it must be intramolecular forces of the single polyquinone chains that are responsible for the better mechanical properties of the elastomeric networks.[7] The single chains do this by relieving the imposed stress dynamically as they decrease their entropies while crosslinked to the rubbery chains at both ends.[3] As seen in Figure 1, the polyquinone chains consist of a series of either benzenoid or quinonoid nuclei or both. These nuclei are planer in nature and changes about the bond angles or the torsional angles within the single nuclei are highly unlikely. The only types of motion these materials might therefore perform must involve bonds connecting the different nuclei. Torsion and/or quinonoid–benzenoid nuclei bending about the connecting bonds are such examples. Nevertheless, the polymeric materials are expected to behave differently in terms of their chemical natures.[8] It is definite that hydrogen bonding developed in polyquinone and polyhydroquinone would have significant roles on their dynamics.

It is the purpose of the current investigation to focus on the chemistry of the polymerization products of p-benzoquinone. The current study elucidates the effects of mild oxidation on the chemical structure of polyquinones as studied using ^{1}H and ^{13}C NMR. It is hoped that the study of the various forms of polyquinones will explain the better protection oxidized polyquinones provide the elastomeric networks over their non-oxidized counterparts. The current investigation attempts to study using molecular dynamics calculations the mechanisms these polymers use in decreasing their entropies in response to the imposed stress. The intramolecular forces of single polyquinone chains are of interest here since they are responsible for the creation of the bimodality of the elastomeric networks. Non-oxidized polyquinone, completely oxidized polybenzoquinone and reduced polyhydroquinone are the subjects of the present investigation. An attempt to reveal the effects of the chemical structures, as deduced using NMR techniques, on the dynamic properties of the chains was made.

EXPERIMENTAL

Methods and Meterials

Polymerization products of p-benzoquinone were prepared as described elsewhere.[5] The cationically prepared materials were repeatedly washed with cold and hot water until free from catalyst, unreacted benzoquinone, hydroquinone, quinhydrone, and the low molecular weight fractions formed. The solid residue was then filtered, dried, and milled to form a deep brown powder.

Oxidation of polyquinone was performed using iodine solution in THF added gradually until oxidation was complete. The oxidized products were then filtered, washed successibely with distilled water and ethanol, dried and milled to form a deep brown powder. A full description of the cationic and anionic polymerization of p-benzoquinone together with the structures, properties, chemical and IR spectral analyses of the non-

oxidized and oxidized products is reported.[5] The mild oxidation of the iodine solution is thus expected to increase the quinonoid/benzenoid ratio up to a certain degree.

NMR Spectroscopy

Liquid state ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AC-250 spectrometer at 250 and 62.5 MHz, respectively. The ^{1}H and ^{13}C NMR experiments were performed on the non-oxidized and oxidized forms of the materials in chloroform-d_1. The chemical shifts of the resulting spectra were all referenced to tetramethylsilane (TMS).

THEORETICAL METHODOLOGY

Molecular Dynamics Simulations

For the molecular dynamics study on the various polymerization products of p-benzoquinone, a simulation model similar to that used by Depner and Schürmann[9] for aromatic polyesters was employed.

The polymer segments are subject to the bond-stretching potential:

$$E_b = \frac{1}{2} k_b (l - l_0)^2$$

where l_0 is the equilibrium bond length, and k_b is the bond stretching constant. The deformation of the bond angle θ between successive pairs of bonds from its equilibrium value θ_0 is governed by the potential:

$$E_\theta = \frac{1}{2} k_\theta (\cos \theta - \cos \theta_0)^2$$

with k_θ being the bond-bending constant. The torsional potential is modeled as

$$E_\phi = K_\phi [1 + \cos(n\phi - \tau)]$$

where k_ϕ is the torsional constant, height of the energy barrier, n is the periodicity, τ is the phase angle. Out-of-plane deformations modeled as a special case of the torsion equation with $\tau = 0$ and $n = 2$ and given by[10]:

$$E_x = K_x [1 + \cos(2\phi)]$$

The out-of-plane potential keeps the connected atom in the plane defined by the other three atoms. This is especially useful when considering the carbon atoms of the aromatic planer nuclei. K_x is the out-of-plane deformation constant. Non-bonded Lennard–Jones interactions between atoms separated by more than three bonds are given by:

$$E_{nb} = 4\varepsilon^* \left[\left(\frac{r^*}{r_{ij}} \right)^{12} - \left(\frac{r^*}{r_{ij}} \right)^6 \right] + C$$

The Lennard–Jones parameters between different atoms A and B are assumed to satisfy the Lorentz–Berthelot mixing rules defined by

$$r_{AB}^* = (r_A^* + r_B^*)^{1/2}$$

and

$$\varepsilon_{AB}^* = (\varepsilon_A^* \varepsilon_B^*)^{1/2}$$

Table I. Partial charges of various atoms comprising the polymerization products of p-benzoquinone (numbers are in accordance with Figure 2)

Atom number	Partial charge	Atom number	Partial charge
q_1	−0.1268	q_{13}	0.4241
q_2	0.1268	q_{14}	0.000
q_3	−0.1268	q_{15}	0.3964
q_4	0.1268	q_{16}	−0.3964
q_5	0.0265	q_{17}	−0.1268
q_6	−0.4506	q_{18}	0.1268
q_7	0.4241	q_{19}	−0.1268
q_8	0.000	q_{20}	0.1268
q_9	−0.1268	q_{21}	0.3964
q_{10}	0.1268	q_{22}	−0.3964
q_{11}	0.0265	q_{23}	−0.1268
q_{12}	−0.4506	q_{24}	0.1268
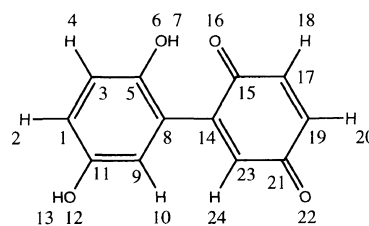
Figure 2. Polyquinone residue numbered in accordance with the partial charges of Table I.
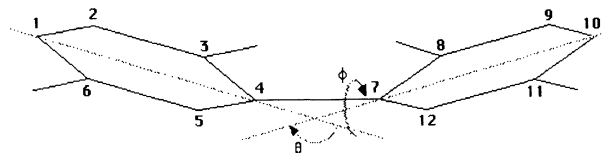
Figure 3. Schematic drawing representing the angles of interest when evaluating the dynamics of a system. The average bending angle, θ, identified by the two lines connecting atoms 1 and 4 and atoms 7 and 10, respectively, and the average torsional angle, ϕ, defined by the four atoms 3, 4, 7, and 10.

Electrostatic interactions between atoms carrying partial charges are given in terms of standard Coulomb representation[11]:

$$E_{ij} = \frac{q_i q_j}{4\pi\varepsilon r_{ij}}$$

where q_i and q_j are the partial atomic charges on atoms i and j, respectively, r_{ij} is the distance between them, and ε is the dielectric constant. The partial charges q_i and q_j were calculated according to:

$$q_i = \sum_j \delta_{ij}$$

where δ_{ij} is the bond increment between the atom i whose partial charge is under evaluation and the other atoms to which the atom i is bonded. The partial charges calculated using the above method is listed in Table I. The hydrogen bond potential is given by[10]:

$$E_{hb} = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{10}}$$

A and B are coefficients with units of $kcal\,mol^{-1}\,Å^{12}$ and $kcal\,mol^{-1}\,Å^{10}$ respectively. r_{ij} is the distance between the atoms i and j in angstroms.

The systems studied are polyquinone (AQ), polyhydroquinone (HQ), and polybenzoquinone (BQ). In case of the last two systems, completely reduced and oxidized forms of the polyquinone were used, to focus on the effects of the reduction and oxidation used to prepare these materials. These methods might not be able to produce completely reduced or oxidized forms. Each polymeric chain consists of six consecutive nuclei of the type corresponding to the polymer under consideration. Polyhydroquinone, for example, consists of all benzenoid nuclei (hydroquinone units) whereas polybenzoquinone consists of all quinonoid ones. Polyquinone naturally consists of both types arranged randomly, Figure 1. An 'all-atom' force field was used, i.e., all the hydrogen atoms were all explicitly considered. No Periodic boundary conditions were imposed since it was the intramolecular force of the single chain under consideration. Newton's equations of motion of polymer segments were integrated[12] using the Verlet algorithm[13] with small finite time steps ($\Delta t = 0.5 \times 10^{-15}$ s). This was done to ensure a reliable representation of the trajectories. For every

structure, simulations were run several times (usually 4 runs) for better averaging. The equilibrium molecular dynamics simulation were usually performed using microcanonical ensembles at a temperature of 298 K. All parameters pertaining to the simulations of polyquinones were previously reported.[10,12,14,15]

Molecular Mechanics and Energy Minimization

Energy minimization of various conformations of the polymerization products of p-benzoquinone was performed using the steepest descent and dynamic quenching methods. In the former, the direction of the line search (the search for a newly lower-energy conformation by changing the coordinates of the atoms) is taken as the current derivative or gradient. After each line search, the old direction is replaced with the gradient at the new point.[16,17] The latter involves coupling the system to a thermal bath,[18] in order to vary the temperature. This is simulated by constantly monitoring and adjusting the average kinetic energy of the atoms to maintain a newly given temperature during a molecular dynamics run. By setting the target temperature to a very low value (e.g., 1 K) the system overcomes small barriers during the relaxation procedure and to finally settle in a lower-energy minimum.

Nuclei Bending, Torsion, and Mean Square Displacements

Since torsions of four body systems as well as bending of three body systems within various nuclei comprising the chains are highly unlikely, only changes about the bonds connecting the different nuclei are considered. Two primary factors are of interest here, the bending and the torsion of the consecutive nuclei with respect to each other. Figure 3 shows a schematic drawing of the two angles under consideration. The nuclei bending angle (θ) is the angle between the two vectors connecting the carbon atoms of each nucleus in the *para* position with respect to the carbon atoms of the bond connecting the two nuclei. In the figure, θ is the angle between the two lines connecting atoms 1 and 4, and atoms 7 and 10, respectively. The nuclei torsional angle (ϕ), alternatively,

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is the torsional angle defined by the four atoms 3, 4, 7, and 8 in the figure.

Mean square displacements were evaluated for each structure after performing the dynamic quenching calculations. Mean square displacements averaged over all atoms with respect to the last time step were only considered. This was chosen to detect dynamics transitions accompanied by the slow down of the system's dynamics in response to lowering the temperature and

subsequently the average kinetic energy of the polymer segments. Minimized structures of the polymerization products were exclusively used as starting configurations of the molecular dynamics runs.

RESULTS AND DISCUSSION

NMR Measurements

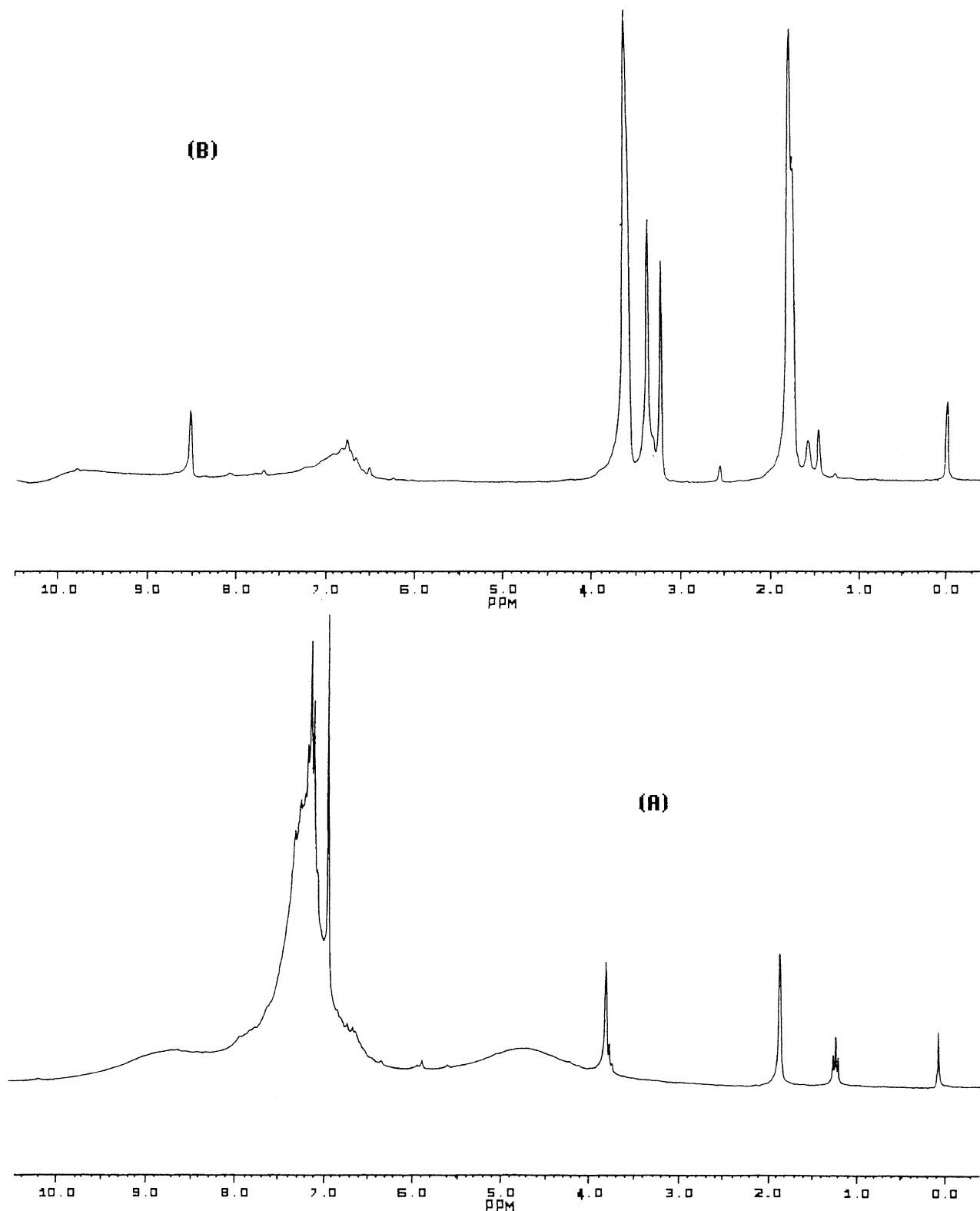Spectra resulting from ^{1}H and ^{13}C NMR studies of

Figure 4. ^{1}H NMR spectra of (A) polyquinones and (B) polybenzoquinones.
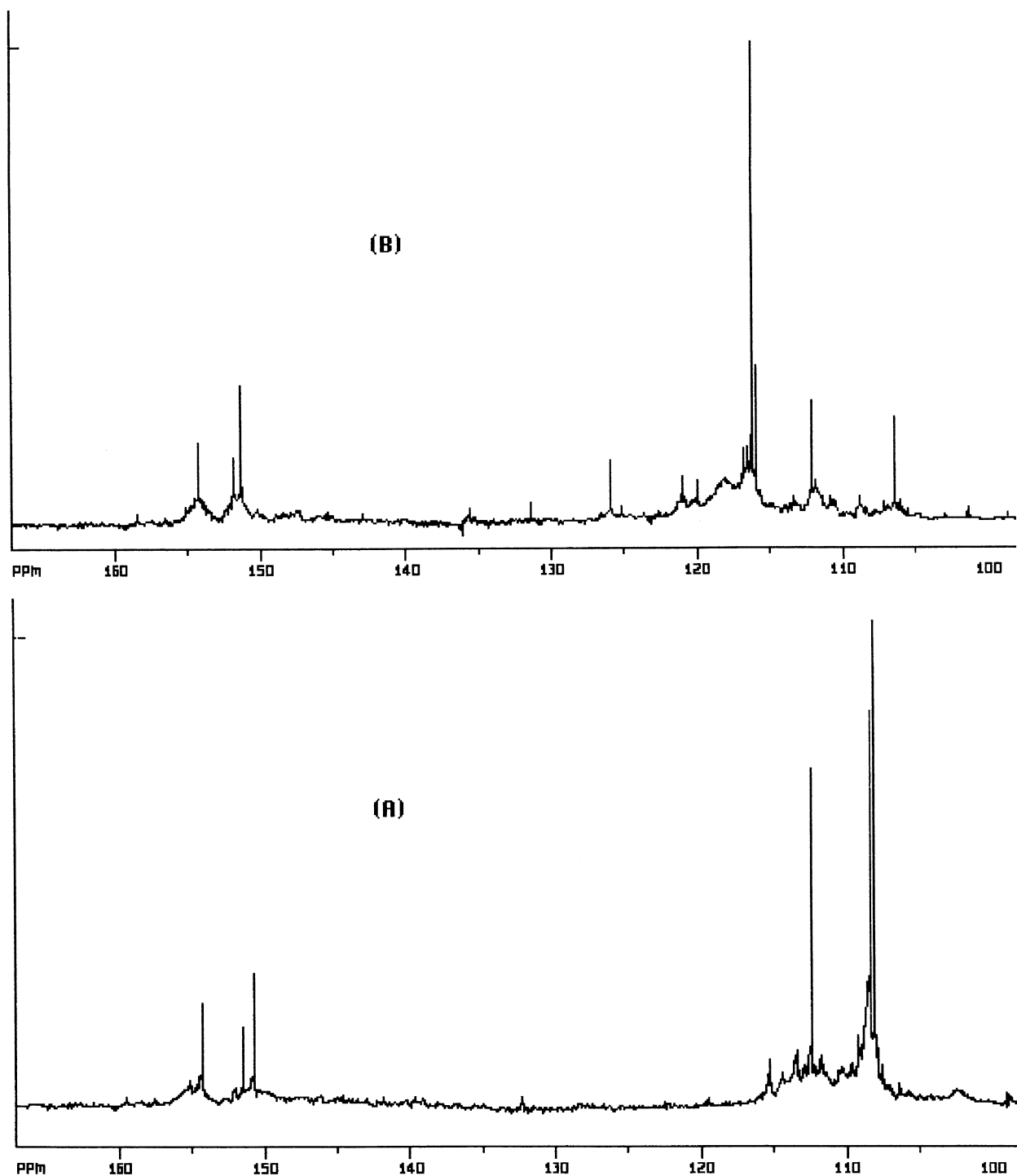
Figure 5. ^{13}C NMR spectra of (A) polyquinones and (B) polybenzoquinones.

the non-oxidized and oxidized polyquinones are represented in Figures 4 and 5, respectively. The (A) sections of the figures refer to the non-oxidized products whereas the (B) sections refer to the oxidized ones prepared using the mild oxidation of iodine solution. In Figure 4, the various peaks appearing in the range of δ 6.0 to δ 8.0 and characterizing the protons attached to aromatic benzene rings (benzenoid nuclei) as well as hydrogen atoms of the hydroxyl groups on these benzenoid structures disappeared upon oxidation. Alternatively, peaks appearing at δ 1.695 and δ 3.568 characterizing protons attached to quinonoid nuclei are seen to have grown substantially. The above observation

is synonymous with the oxidation of benzenoid nuclei into quinonoid ones. Obviously, the quinonoid/benzenoid ratio has been altered as a consequence of the oxidation process. Similar conclusions could also be deduced from ^{13}C NMR observed signals, Figure 5.[19] The peaks appearing in the range of 105 ppm to 115 ppm are assigned to the proton attached carbon atoms. The peaks at 151.29, 151.81, and 154.14 ppm were assigned, alternatively, to the non-proton attached carbon atoms. The decline of the peaks in the range of 105—115 ppm upon oxidation also indicates the loss of the benzenoid structures oxidized into the alternative quinonoid ones. The peaks at 116 ppm are probably due to the carbon–

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carbon double bond structures such as quinonoid nuclei present after the oxidation is complete. The slight change of peaks appearing after the 150 ppm indicates that no further modification of the structure of the compounds has taken place. In general, no degradation of the quinonoid or benzenoid structures has taken place as a consequence of the mild oxidation of the iodine solution as was the case with strong oxidants such as the permanganate solutions.[1]

Molecular Mechanics and Energy Minimization

Energy minimization of the three macromolecular structures was performed using steepest descent and dynamic quenching methods. The polymers under study are polyquinone (AQ), polyhydroquinone (HQ), and polybenzoquinone (BQ). Potential energies of totally minimized structures using these two methods are given in the first two columns of Table II, respectively. Schematic snapshots of the minimized structures taken after the minimization was complete according to the above mentioned methods are shown in figures 6 and 7, respectively. Data shown in the table and the figures indicate that the quenching technique, as expected, was able to overcome the small barriers between the stable points on the potential energy surface to finally approach a new energy minimum. Results shown in the table also indicate that polyquinone and polyhydroquinone are greatly stabilized by the presence of the hydrogen bonding which also might limit the number of conformations.

Studying the effect of cooling on the system behavior, results for the average bending angle, average torsion angle and mean square displacements are shown in Figures 8 through 10, respectively. Table III also represents some statistical information regarding the bending and torsion of the different chemical formula. In general, nuclear bending is more restricted than the torsion causing the range of the former to be much smaller than that of the latter. The dynamics of bending must therefore require more energy and upon cooling the system dynamics loses most of the energy available through the more restricted bending fluctuations. Polyhydroquinone being mostly stabilized by hydrogen bonding shows the highest bending movement, Figure 8. The presence of the hydrogen bonds between the hydroxyl groups on neighboring hydroquinone nuclei should restrict to some extent the torsional movement of these nuclei about the bonds connecting them. This

is particularly shown in Figure 9 by the steady behavior of the polymer at lower temperatures. The ease of torsional movement of polybenzoquinone is due to the lack of any hydrogen bonding which leads to a moderate
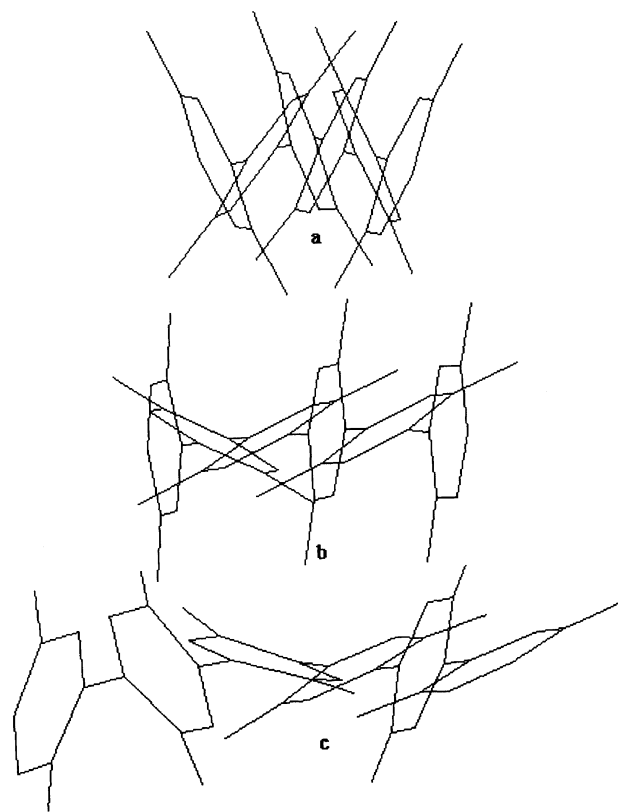

Figure 6. Photographs of the low energy conformations of the polymerization products of p-benzoquinone as minimized using steepest descents procedure, see legend for Figure 1.
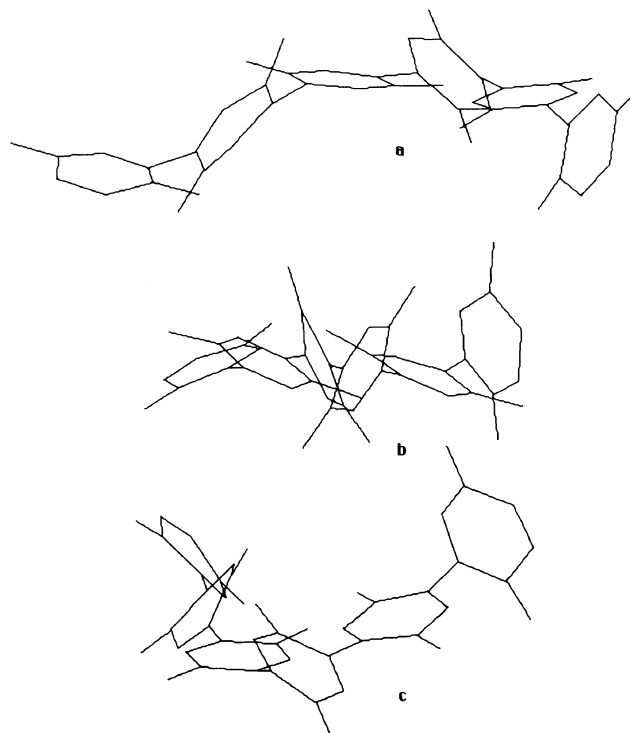

Figure 7. Photographs of the low energy conformations of the polymerization products of p-benzoquinone as minimized using dynamic quenching technique, see legend for Figure 1.

Table II. Potential energies of chemically different polymerization products of p-benzoquinone studied using energy minimization and molecular dynamics procedures

	Total potential energy/kcal mol^{-1}		
	Energy minimization[a]		Molecular dynamics[b]
Entry	Steepest descent	Dynamic quenching	
AQ	40.723	37.187	105.421
HQ	−0.543	−8.9010	71.147
BQ	76.749	74.179	103.69

[a] Data correspond to the minimum energy conformations. [b] Data taken at the vicinity of room temperature (298 K).

Table III. Statistics of bending and torsional dynamics of chemically different polymerization products of p-benzoquinone in energy minimization

| | Minimun degrees | | Maximun degrees | | Range degrees | | Mean degrees | | S.D.[a] | | S.E.[b] | |
	Bnd[c]	Tor[d]	Bnd[c]	Tor[d]	Bnd[c]	Tor[d]	Bnd[c]	Tor[d]	Bnd[c]	Tor[d]	Bnd[c]	Tor[d]
AQ	169.9	148.4	175.8	164.9	5.838	16.42	173.1	157.6	1.359	4.042	0.248	0.738
HQ	169.6	165.1	176.3	183.2	6.704	18.15	173.4	178.0	1.838	4.592	0.336	0.838
BQ	170.4	219.5	174.9	227.9	4.517	8.417	173.4	223.7	1.304	2.395	0.238	0.437

[a] S.D., standard deviation. [b] S.E., standard error. [c] Bnd, bending. [d] Tor, torsional.
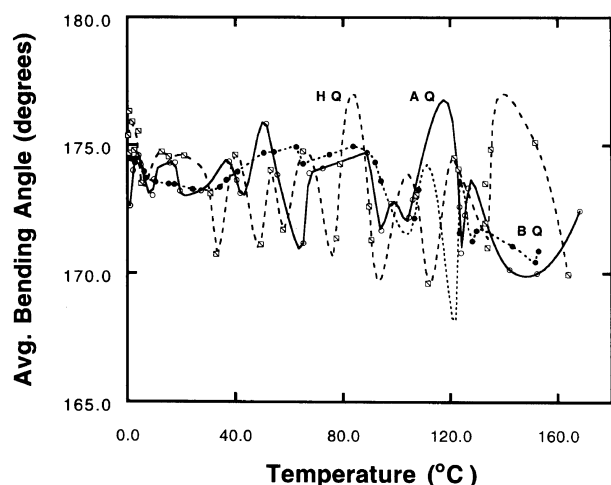

Figure 8. Average bending angle of the three chemically different polymerization products of p-benzoquinone as a function of temperature.
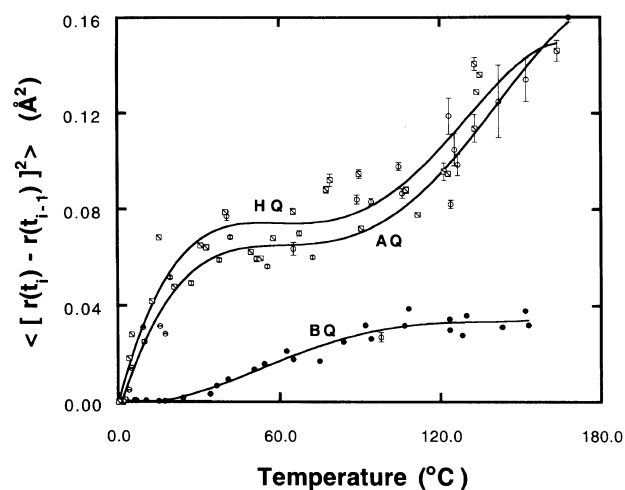

Figure 10. Average mean square displacements of the three chemically different polymerization products of p-benzoquinone as a function of temperature.
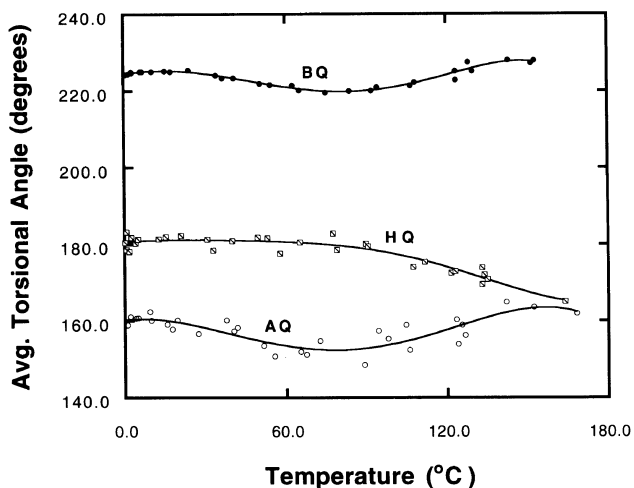

Figure 9. Average torsional angle of the three chemically different polymerization products of p-benzoquinone as a function of temperature.

fluctuation of its bending behavior, Figure 8, and more energetic torsion, Figure 9. The dynamics in general of polybenzoquinone are much more restricted than that of polyquinone and polyhydroquinone as shown in Figure 10. Not as much as the case with polyhydroquinone, the torsion of polybenzoquinone is somewhat restricted as well. This is because of the partial negative charges carbonyl oxygen atoms might carry, Table I. The maximum repulsion between these charged atoms must then take place as the torsional angles approach 180°.

Alternatively, torsional angle value of polyhydroquinone is near the 180°. This favors the hydrogen bonding formation between neighboring groups. Because of the existing repulsion between the carbonyl oxygen atoms, this value might either go up or down as the case with polybenzoquinone and polyquinone with the high energy barriers at the 180°. These barriers must therefore be high enough not to be easily overcome and fluctuations between these barriers are therefore only allowed, Figure 9. Polyquinone in general, shows behavior inbetween that of polyhydroquinone and polybenzoquinone. The behavior is, however, more closely related to that of polyhydroquinone which indicates the stronger presence of the benzenoid nuclei over the quinonoid ones in an equimolar ratio compound. This is probably because of the more restricted dynamics of the quinonoid nuclei in general. In all three models, the mean square displacement calculations, Figure 10, show a transition temperature at 92°C at which all three systems slow down in molecular dynamics.

Molecular Dynamics

The molecular dynamics of the three systems under study are reported in Figures 11 and 12. In the figures, the behavior of polybenzoquinone is quite different from the two closely related behavior of polyhydroquinone and polyquinone. The same arguments thus described above should apply in this case as well. Average potential energies of the three systems calculated at room temperature are given in the third column of Table II.
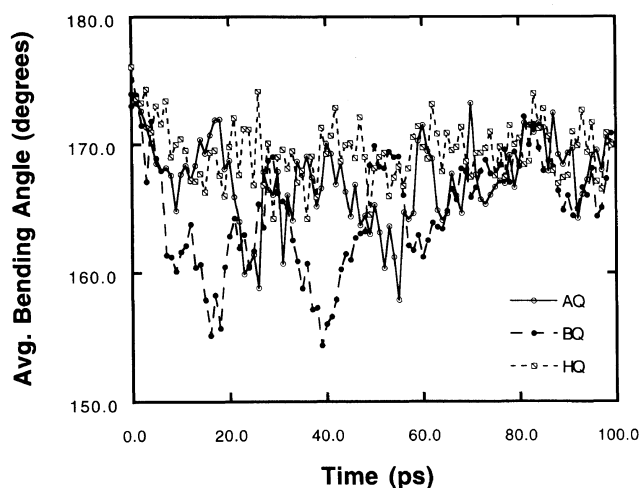
Figure 11. Average bending angle of the three chemically different polymerization products of p-benzoquinone as a function of time. System dynamics were calculated at the room temperature of 298 K.
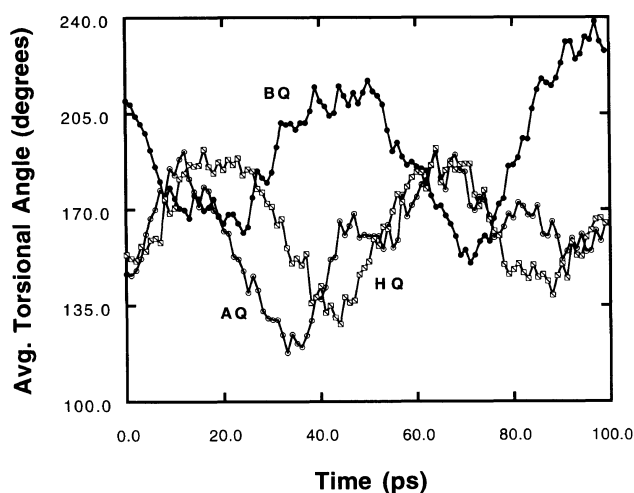

Figure 12. Average torsional angle of the three chemically different polymerization products of p-benzoquinone as a function of time. System dynamics were calculated at the room temperature of 298 K.

Polyhydroquinone is shown to have the least potential energy due to the presence of hydrogen bonding. This extra stability might however limit the number of accessible conformations available to the polymer and be responsible for its stiffness and lower mobility. Polybenzoquinone is expected to show more energetic

dynamics compared to the other two systems. This is due to the repulsion present between the negatively changed carbonyl oxygen atoms and the lack of any stabilizing hydrogen bonding as well. This is observed when considering the average bending dynamics of the nuclei. Nuclei comprising polybenzoquinone show more bending fluctuations than others since it naturally requires more energy to take place than torsion. The polymeric chains of polybenzoquinone must therefore be more elastic in nature with a greater number of conformations available.

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