s^{-1}, at least comparable to the rates of excimer formation in polymers with similar chain structures. However, polystyrene, with one of the highest values of k_{DM}, has an anomalously slow rate of relaxation. It is clear that further studies must be made before firm conclusions should be drawn on this aspect of the phenomenon.

Acknowledgment. The authors are grateful to the National Research Council of Canada for scholarship support (to J.S.A.) and for financial support of this research. They also wish to acknowledge the many helpful and stimulating discussions with T. L. Nemzek, C. E. Hoyle, and D. A. Holden.

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Polymer Reaction. 11. Oxidative Pyrolysis of Poly(isoprene)[1]

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ABSTRACT: Poly(isoprene) has been oxidized at temperatures between 268 and 340 °C. The products were GC separated and on-line identified by an interfaced GC pyrolysis peak identification system. The most abundant products are methyl ethyl ketone, methyl vinyl ketone, and butyraldehyde, with lesser amounts of acetaldehyde, acetone, methacrolein, propionaldehyde, acrolein, and formaldehyde. A free-radical chain mechanism is proposed. The rate constants for the oxidative pyrolysis of poly(isoprene) have been determined; the overall activation energy is about 27 kcal/mol.

We have constructed an interfaced GC pyrolysis peak identification system for the investigation of high-temperature reactions of polymers with on-the-fly analysis of products. The pyrolyses of poly(propylene)[3] and poly(isoprene)[4] in a stream of He carrier gas were found to be different from studies made in vacuo or in a stagnant inert atmosphere. Oxidative pyrolysis of poly(propylene) had also been investigated[5] with this system. Reaction mechanisms were formulated from the products and their distributions. It was found that the kinetics of oxidative degradation at temperatures between 240 and 289 °C can be calculated from rate constants determined for autoxidation between 71 and 140 °C.[6,7]

Our recent interests have been concerned with polymer degradation and stabilization associated with its combustion and flame retardancy. Therefore, even though there have been a number of reports on the aging and autoxidation of poly(isoprene) in the vicinity of 100 °C, data at much higher temperatures are scarce. The central purpose of this work is to determine the rates of oxidative degradation of poly(isoprene) at high temperatures, to remove the products rapidly from the reaction zone by a carrier gas thus simulating the conditions for a burning polymer, and to identify these oxidation products.

Experimental Section

The poly(isoprene) used in this study contains 97% cis-1,4 and 3% 3,4 structural units. It is the product of Goodyear (Natsyn 2200) with a number average molecular weight of about 200 000. The in-process phenolic antioxidant was removed by repeated dissolution in toluene and reprecipitation with acetone and vacuum dried.

The pyrolysis temperatures were determined by TGA (DuPont 900 thermal analyzer) in air at a flow rate of 25 mL min^{-1} and a heating rate of 30 °C min^{-1}. To investigate its ignition char-

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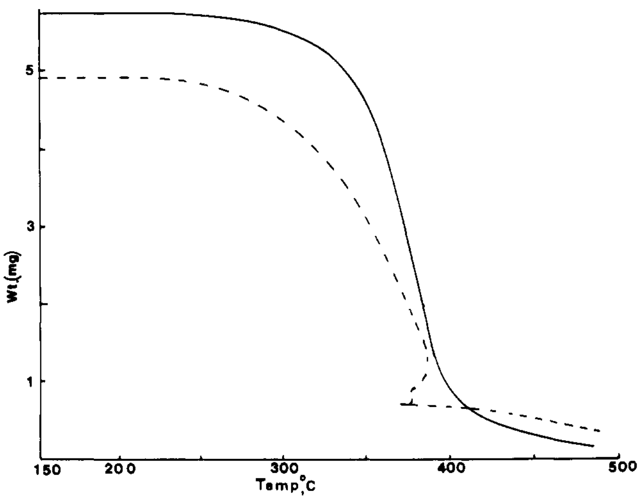


Figure 1. Thermogravimetric analysis thermogram of poly(isoprene) in air with a flow rate of 25 mL min^{-1} (—) and 60 mL min^{-1} (- - -). The heating rate is 30 °C min^{-1}.

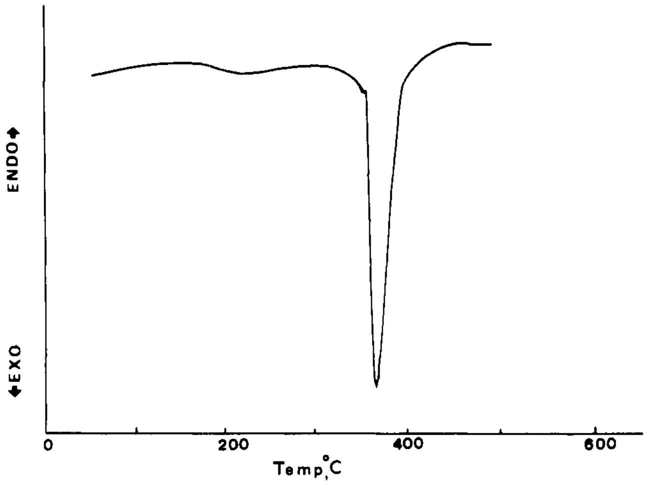


Figure 2. Differential thermal analysis thermogram of poly(isoprene) in air with a flow rate of 60 mL min^{-1}. The heating rate is 30 °C min^{-1}.

acteristics, the experiment was repeated at an air flow rate of 60 mL min^{-1} at the same heating rate. The result was compared with that of DTA (plug-in module for DuPont 900 thermal analyzer) under similar conditions.

About 6 mg of sample was used in each experiment. The polymer was oxidized in a SPEX MP-3 thermal analyzer with an air flow rate of 25 mL min^{-1} at 268, 290, 315, and 340 °C. A detailed description of the equipment has been given previously.[8] A Chromosorb 102 column (12 ft × $^1/_8$ in. o.d.) was used to separate the products with flame ionization detection. The products were identified by mass spectrometry.

The total reaction rate was taken to be proportional to the weight loss of poly(isoprene). This was determined by subjecting a weighed sample of about 6 mg to a preset temperature for a certain length of time followed by rapid quenching and reweighing.

Results

In order to determine the proper temperature range for experimentation, thermogravimetric analysis of poly(isoprene) was performed. At an air flow rate of 25 mL min^{-1}, the polymer oxidizes relatively slowly below 200 °C (Figure 1). At ca. 450 °C, the polymer has completely oxidized into volatile products. When the flow rate was increased to 60 mL min^{-1}, the thermogram shows a characteristic ignition point at about 385 °C. Corresponding to this is the strong exotherm in the differential thermal analysis thermogram (Figure 2).

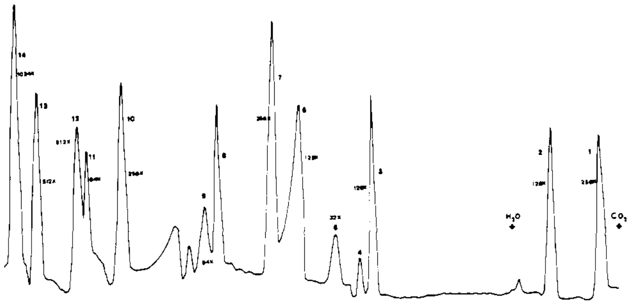


Figure 3. Low boiling pyrogram of poly(isoprene) at 388 °C in air.

Table I
Fragmentation Patterns of Products from Oxidative Pyrolysis of Poly(isoprene) at 388 °C

peak no.	product	fragmentation pattern
	carbon dioxide[a]	$\underline{44}$, 28
1	ethylene	$\underline{28}$, 27, 26
2	ethane	30, 29, $\underline{28}$, 27, 26
	water[a]	$\underline{18}$, 17, 16
3	propylene	42, $\underline{41}$, 39, 27
4	propane	44, 43, $\underline{29}$, 28, 27
5	formaldehyde	30, $\underline{29}$, 28
6	methanol	32, $\underline{31}$, 29, 15
7	acetaldehyde	44, 43, 42, $\underline{29}$
8	acrolein	56, $\underline{41}$, 39, 27
9	propanal	58, $\underline{43}$, 41, 29
10	acetone	58, $\underline{43}$, 28
11	methacrolein	70, $\underline{55}$, 41, 39, 29
12	methyl vinyl ketone	70, 68, $\underline{67}$, 53, 42, 41, 40, 29, 27
13	butanal	72, 50, 42, $\underline{41}$, 39, 29
14	methyl ethyl ketone	72, $\underline{55}$, 43, 42, 39, 27

[a] Detected by MS.

Table II
Kinetic Results of the Oxidative Pyrolysis of Poly(isoprene)

temp, °C	apparent rate const, s^{-1}
268	4.0×10^{-4}
290	6.3×10^{-4}
315	4.0×10^{-3}
340	5.8×10^{-3}
activation energy,[a] kcal mol^{-1}	27

[a] The energy of activation was found from the Arrhenius plot (Figure 6) to be about 27 kcal mol^{-1}.

The pyrolysates were separated with a Chromosorb 102 column (Figure 3), and each peak was identified by mass spectrometry (Table I). The attenuation factors are shown by 4×, 8×, etc., alongside each peak which are also numbered sequentially. The GC detector sensitivity has not been determined for each of the products, so their relative abundance may be ranked only semiquantitatively. The most abundant products are methyl ethyl ketone, methyl vinyl ketone, and butyraldehyde followed by acetaldehyde, acetone, and ethylene. The next group contains ethane, propylene, methanol, propionaldehyde, methacrolein, acrolein, and formaldehyde. In Table I the most abundant ion species are underlined.

The loss of polymer through oxidative degradation has been determined from 268 to 340 °C (Figure 4). From semilog plots of the data (Figure 5), the apparent rate constants were obtained, and the values of the rate constants are given in Table II.

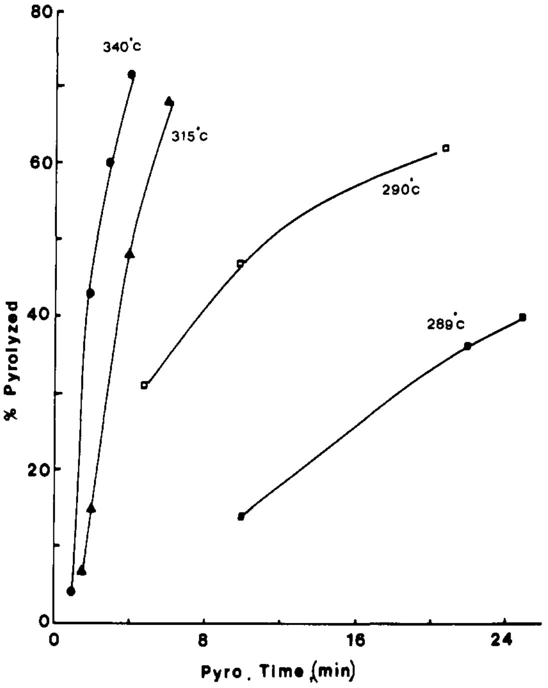


Figure 4. Rate of oxidative pyrolysis of poly(isoprene) in air.

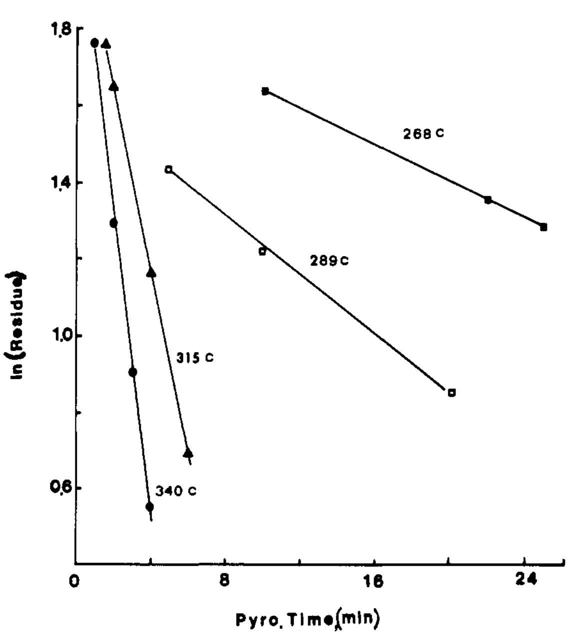


Figure 5. Semilog plots for oxidative pyrolysis of poly(isoprene) in air.

Discussion of Results

Autoxidation of poly(isoprene) at temperatures between ambient and 140 °C has been much investigated in the past. Bolland and Hughes[9] obtained results suggesting that the primary oxidation product of gutta–persha is a cyclic peroxide–hydroperoxide. At these temperatures, the low molecular weight oxidation products are carbon dioxide, formaldehyde, and acetic acid[10] formed in 2:1:1 ratio. Bevilacqua et al.[11] identified levulinaldehyde as the other major volatile product. Combination of these observations led to Scheme I.[11]

With the advent of GC, additional products were identified[12] through infrared and dinitrophenylhydrazone derivatives: CO, acetaldehyde, methyl formate, propionaldehyde, acetone, methanol, 2-methylfuran, methacrolein, ethanol, methyl ethyl ketone, methyl vinyl ketone, and water. Reaction mechanisms were proposed for the formation of some of the products from either levulinaldehyde or other intermediates, all of which involve multistep processes. More recently, Morand[12] performed oxidation of poly(isoprene) and identified about 23 products. They were assumed to be produced by the mechanism suggested by Bevilacqua et al.[11]

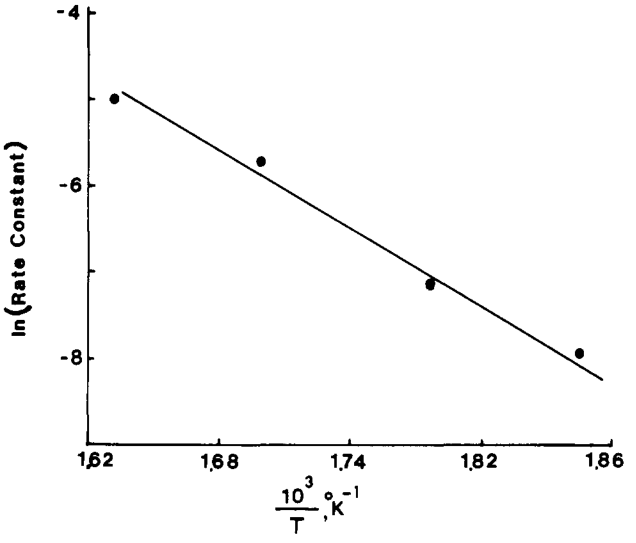
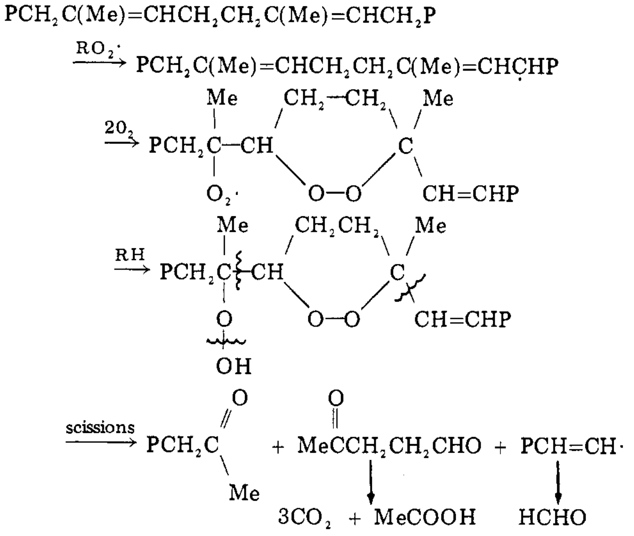


Figure 6. Arrhenius plot for oxidative pyrolysis of poly(isoprene) in air.

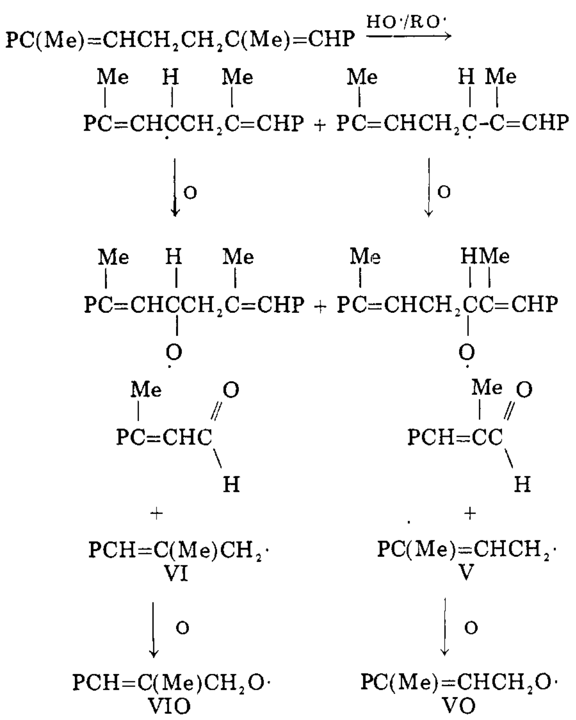
Scheme I



Our experimental temperatures were much higher than those used in previous studies, and oxidations should proceed at correspondingly faster rates. One must be concerned, therefore, with factors which may complicate the reaction pathways: how significant are secondary reactions and oxygen diffusion limitations? Incidentally, these questions should also be raised for autoxidations even at 100 °C but unfortunately were seldomly asked.

It has been firmly established by our previous studies[13] that oxygen starvation is virtually unavoidable in any accelerated autoxidation of solid polymer samples. This is simply because at any locus where autoxidation took place, there is by definition a lowering of oxygen concentration until it is replenished by diffusion of oxygen. Autoxidation of a solid polymer specimen, such as poly(propylene),[13] is confined to the surface layer to a depth of ca. 0.1 mm. Decreasing the particle size of the sample and increasing the oxygen pressure reduces oxygen diffusion limitation but does not eliminate it; increasing the

Scheme II



Scheme III

$$\mathrm{VO} \longrightarrow \mathrm{PCH_2C(Me){=}CH\cdot\ (III)} + \text{formaldehyde} \xrightarrow{1\text{-}3} \mathrm{P{=}CHCH_2CH_2\cdot\ (I)} + \mathrm{MeC(H){=}CHCHO} \xrightarrow{5\text{-}1} \mathrm{III} + \mathrm{MeO\cdot} \longrightarrow \text{methanol}$$

$$\mathrm{VIO} \longrightarrow \mathrm{PCH_2CH{=}C(Me)\cdot\ (II)} + \text{formaldehyde} \xrightarrow{1\text{-}3} \mathrm{P{=}C(Me)CH_2CH_2\cdot\ (IV)} + \text{methacrolein}$$

Scheme IV

$$\mathrm{IO} \longrightarrow \mathrm{V} + \text{formaldehyde} \xrightarrow{1\text{-}2} \mathrm{III} + \text{acetaldehyde}$$

$$\mathrm{IIO} \longrightarrow \mathrm{VI} + \text{vinyl methyl ketone} \xrightarrow{7\text{-}2} \text{polymeric olefin} + \mathrm{MeC(O)CH_2CH_2\cdot} \longrightarrow \text{butanone}$$

$$\mathrm{IIIO} \xrightarrow{4\text{-}2} \text{polymeric olefin} + \mathrm{MeC(H)CHO} \longrightarrow \text{propionaldehyde} \longrightarrow \mathrm{V} + \text{methacrolein} \xrightarrow{3\text{-}2} \mathrm{I} + \text{acrolein}$$

$$\mathrm{IVO} \longrightarrow \mathrm{VI} + \text{formaldehyde} \xrightarrow{1\text{-}2} \mathrm{II} + \text{acetaldehyde}$$

Scheme V

$$\mathrm{ROOH} \xrightarrow{k_1} \mathrm{RO\cdot} + \mathrm{\cdot OH}$$

$$\mathrm{RO\cdot} + \mathrm{RH} \xrightarrow{k_2} \text{products} + \mathrm{R\cdot}$$

$$\mathrm{R\cdot} + \mathrm{O_2} \xrightarrow{k_3} \mathrm{RO_2\cdot}$$

$$\mathrm{RO_2\cdot} + \mathrm{RH} \xrightarrow{k_4} \mathrm{ROOH} + \mathrm{R\cdot}$$

$$\mathrm{2RO_2\cdot} \xrightarrow{k_5} \text{products (nonvolatile)}$$

temperature aggravates the limitation. In our oxidative pyrolysis of poly(isoprene), the isolation of hydrocarbon products such as ethane, ethylene, and propylene suggests oxygen diffusion limitation even through there was a rapid flow of air above the very thin specimen. In the case of oxidation of poly(propylene),[5] hydrocarbon product yields decreased with increasing oxygen partial pressure in the carrier gas but were not entirely suppressed even with pure oxygen as the carrier.

Secondary oxidation processes also cannot be easily avoided under the above experimental conditions. The principal product of successive oxidations is CO_2, whose yield increases with increasing oxygen concentration. The yields of all of the carbonyl products increase rapidly at first with the increase of oxygen partial pressure. This is followed by a rapid decline in yield with the further increase in oxygen concentration suggesting the occurrence of secondary oxidations. The level of oxygen used in the present study is sufficiently high so that all of the products, excepting CO_2 of course, have declined in their yields from the maxima observed at lower oxygen partial pressures. However, the objective of the work is not to confine autoxidations to the primary step but to simulate those conditions which might be prevalent in the molten region of a burning polymer. Since it is the volatile oxidation products which are fed into and sustain the combustion, we have focused our attention on them.

All of the major oxidation products of poly(isoprene) (Table I) may be accounted for by a free-radical mechanism, portions of which have been invoked by various investigators before. The initiation process is the homolysis of a hydroperoxide.[9] The hydroxy and alkoxy radical abstracts an allylic hydrogen and, followed by oxygenation, produces allylic radicals V and VI and then the corresponding oxy radicals VO and VIO. Propagation reactions of radicals VO and VIO by hydrogen abstraction lead to some of the observed compounds (italic) as well as alkyl radicals I and IV and vinyl radicals II and III. In Scheme III the numbers above the arrows indicate the carbon atoms involved in the hydrogen abstraction. Oxygenation converts the alkyl and vinyl radicals to their corresponding oxy radicals. Analogous propagation reactions lead to the other identified oxidation products (Scheme IV). Finally, from a resonance form of allylic radical VI, acetone can be derived.

The termination reaction almost certainly involves peroxy and alkoxy radicals in the usual manner.

In addition to those propagations leading to volatile products, similar processes also occur to cause scission, giving polymeric radicals. The oxygen consumption to the chain scission ratio has been determined and was found[10,11] to decrease from 40 at 25 °C to 16 at 110 °C. A plot of this ratio to T^{-1} gave a linear Arrhenius relationship. Extrapolating to the temperature regions of this work, we find that the oxygen consumption to scission ratio is about 5 to 6. Undoubtedly, less volatile products such as levulinaldehyde are also produced in oxidative pyrolysis. They would be very susceptible to secondary oxidations since they are not as readily transported away by the carrier gas into the trap.

The overall kinetics of oxidative degradation may be represented by the simplified reaction sequence in Scheme V. The products of termination of the peroxy radicals are considered to be nonvolatile. It is not possible to include explicitly both oxygen diffusion limitation and secondary oxidations. However, the two processes have opposite dependencies on oxygen partial pressure. If one neglects their complicating contributions, then a pseudo-steady-state treatment gives

$$\frac{d[\text{product}]}{dt} = \frac{-d[\mathrm{RH}]}{dt} = k_4\left(\frac{k_1[\mathrm{ROOH}]_s}{k_5}\right)^{1/2}[\mathrm{RH}] \quad (1)$$

The overall activation energy is $E_4 + {}^1/_2E_1 - {}^1/_2E_5$, which was found to be 27 kcal mol^{-1}. Bolland and tenHave[14] have studied the kinetics of benzoyl peroxide initiated oxidations of model compounds of poly(isoprene). They found an overall activation energy of about 24 kcal mol^{-1} for squalene and 6-dimethylocta-2,6-diene (diisoprene). The difference between the two values may be attributed to the dissociation activation energy of the initiator. The value of E_1 for benzoyl peroxide in the polymer matrix has been accurately determined to be 30 kcal mol^{-1}.[7] Therefore, $E_4 - E_5/2$ is 9 kcal mol^{-1}. Substituting these values, one finds $E_1 \approx 36$ kcal mol^{-1} for poly(isoprene) oxidation. This high activation energy is consonant with the dissociation of a relatively stable peroxide,[9-11] such as the one shown in Scheme I.

Acknowledgment. The authors wish to acknowledge helpful advice from Professor P. C. Uden.

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Conformational Energies and the Random-Coil Configuration of Poly(oxypropylene)

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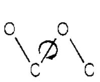
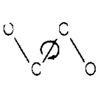
Received May 8, 1979

ABSTRACT: Conformational energies of the poly(oxypropylene), poly(methyloxirane), chains were calculated by using semiempirical potential energy functions. Experimental values of the same energies were also obtained from the rotational isomeric state analysis of the unperturbed dimension, dipole moment, and bond conformations observed for isotactic samples. The magnitude of stabilization energies associated with the gauche O–C–C–O arrangements was estimated from the difference between theoretical and experimental energies thus established. A value of $\Delta E_\alpha = 0.7$ kcal mol^{-1} was obtained for the gauche conformation (α) with the articulated methyl group trans to the preceding oxygen, being in fair agreement with the value (1.0 kcal mol^{-1}) reported previously for the poly(oxyethylene) chain. The gauche oxygen effect was found to be less pronounced for the conformation β in which the preceding oxygen atom is syn to both the following oxygen and the methyl group ($\Delta E_\beta = 0.2 \pm 0.1$ kcal mol^{-1}). Conformational energy parameters thus estimated were used to calculate the characteristic ratio $\langle r^2 \rangle_0/nl^2$, the dipole moment ratio $\langle \mu^2 \rangle/nm^2$, the bond conformations for the skeletal C–C bond, and their temperature coefficients for isotactic, syndiotactic, and atactic chains. The effects of atypical head-to-head and tail-to-tail placements were also examined.

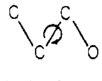
Configuration-dependent properties of polyoxide chains such as $[-(CH_2)_yO-]_x$ have been investigated in a previous paper by one of the present authors and Mark.[2] The most characteristic feature of such polymeric chains is a decisive perference for the gauche conformation over the trans around certain skeletal bonds.[2-8] In poly(oxymethylene) (POM) ($y = 1$), gauche states about an internal



bond are found to be ca. 1.5 kcal mol^{-1} lower in energy than the alternative trans state.[3-5] It has been shown[9] that such conformational characteristics possess some common aspects with the "anomeric effect"[10] known in carbohydrate chemistry. Gauche states for the



bond of poly(oxyethylene) (POE) ($y = 2$) are ca. 0.4 kcal mol^{-1} below the trans state.[3,5-7] For bonds of the type



in poly(oxytrimethylene) (POM_3) ($y = 3$) and poly(oxytetramethylene) (POM_4) ($y = 4$) chains,[3,7,8] preference for gauche states is ca. 0.2 kcal mol^{-1}. Theoretical calculations based on semiempirical conformational energy functions[2,11] failed to reproduce the aforementioned energy differences.

For the POE chain, the theoretical value[2] is 0.6 kcal mol^{-1} in favor of the trans state in opposition to that (–0.4 kcal mol^{-1})[6,7] estimated from the experimental data. Similar energy discrepancies have been observed for various halogenated hydrocarbons.[12] For example, in 1,2-difluoroethane, gauche states which involve the F···F interaction should be disfavored by Coulombic repulsions. They are found, however, to be of essentially the same energy as the alternative trans states.[13] There is no simple explanation for such unusual conformational behavior termed as the "gauche effect", the "hockey-sticks effects", the "gauche-attraction effects", and so on.[14,15]

A similar "gauche oxygen" effect may be expected in the poly(oxypropylene) (POP) chain $[-CH_2CH(CH_3)O-]_x$,

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