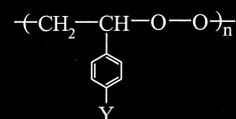


Full Paper: The synthesis and spectroscopic characterization of three polymeric peroxides of styrene monomers with substituents in the *para* position are discussed. NMR spectroscopy revealed the alternating copolymer structure with labile peroxy bonds (—O—O—) in their main chain. The thermal reactivity of the polymers was studied by differential scanning calorimetry and thermogravimetry. The measured heat of degradation of these polymers is nearly the same as that of poly(styrene peroxide). The mechanism of the primary exothermic degradation has been substantiated by thermochemical calculations. The chain dynamics studies of these polyperoxides in terms of ^{13}C spin-lattice relaxation time (T_1) have been carried out to understand their main chain flexibility. The temperature dependence of correlation time has been utilized for the determination of the activation energy for the overall segmental motion and internal group rotation. Their flexibil-

ity in terms of glass transition temperature (T_g) have been examined. The flexibility trend observed in solution parallels that in the bulk.



PPMSP : Y = CH₃

PPBrSP : Y = Br

PPTBSP : Y = C(CH₃)₃

para-Substituted Poly(styrene peroxide)s: Synthesis, Characterization, Thermal Reactivities, and Chain Dynamics Studies in Solution

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Introduction

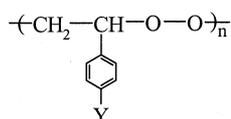
In 1977, Cais and Bovey reported a study of the chain flexibility and molecular dynamics of poly(styrene peroxide) (PSP).^[1] Polyperoxides had previously received attention only with regard to their intermediacy in the inhibition by oxygen of vinyl polymerization.^[2,3] Recently, studies on polymeric peroxides have been successful in providing a thermochemical basis for the unusual exothermic thermal degradation of these polymers.^[4,5] It has resulted in detecting a unique phenomenon of autopyrolysis in PSP, which has made it a candidate for specialized fuels of the future.^[6] The property of autopyrolysis exhibited by these polymers is due to their highly exothermic heats of degradation. Apart from this their technological importance as polymeric thermal^[7] and photo-initiators^[8] for vinyl monomers to synthesize homopolymers and block copolymers, and their applications as curators in coating and molding are well known.^[9]

An evaluation of the heats of degradation of different polymeric peroxides is difficult for lack of data. The number of polyperoxides reported so far is only about two dozen,^[10] and except for very few, they have hardly been characterized. In view of their potential as highly exothermically degrading materials it is desirable to study polyperoxides. By a comparison of the available heat of degradation of PSP^[4] and poly(methyl methacrylate peroxide) (PMMAP),^[5] (the former being higher) it was of interest to synthesize new polyperoxides from aromatic monomers. Hence *para*-substituted styrenes were chosen as monomers for the preparation of polyperoxides.

Studies on the dynamics of polymer chains have attracted considerable interest because chain dynamics play an important role in determining the macroscopic properties of the polymeric systems. Among the various techniques employed for the study of chain dynamics, nuclear magnetic resonance has proved to be a powerful

tool since it selectively allows detailed analysis of the motions of the different components of the polymer chain, at the atomic level. For example, backbone and side group motions or the motion of the different components of a copolymer can be clearly differentiated.^[11,12] Comparative studies of chain flexibility and molecular dynamics among a class of polymers will be very useful in understanding the physical properties and processability of the polymers.^[13] This type of study is rather rare in weak link polymers. Because segmental motions determine the spin-lattice relaxation in reasonably dilute solutions, a comparison of T_1 values provides a measure of the relative barriers to conformational transitions. Some insight into the general steric interactions prevalent in polymer structures may be obtained as they affect the transitions between the conformational states. Such studies have customarily been divided into two regimes: polymer solutions, in which chain motions are relatively fast, and polymers in the solid state, where motional freedom may cover several orders of magnitude. Studies on the chain dynamics in dilute solutions have the advantage that it is possible to focus on the internal motions of a single chain since the effect of inter-chain interactions are minimized.^[14]

In this paper, we present studies on the synthesis, characterization, thermal reactivity, and comparative chain dynamics of three polyperoxides, namely poly(*p*-methylstyrene peroxide) (PPMSP), poly(*p*-bromostyrene peroxide) (PPBrSP) and poly(*p*-*tert*-butylstyrene peroxide) (PPTBSP) having the following general structure:



PPMSP : Y = CH₃

PPBrSP : Y = Br

PPTBSP : Y = C(CH₃)₃

Dulog et al. reported the synthesis of PPMSP and PPBrSP but their spectral characterization have not been made.^[15] Both PPTBSP and PPBrSP are powdery materials, thus they are easier to handle compared to the PPMSP and PSP, which are sticky semisolids under ambient conditions.

Experimental Part

Materials

p-Methylstyrene (PMS) (Lancaster, England), *p*-bromostyrene (PBrS) (Aldrich, USA) and *p*-*tert*-butylstyrene (PTBS) (Lancaster, England) were freed from inhibitor by washing

with 5% NaOH and then with water several times. After drying over anhydrous Na₂SO₄, they were distilled under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN) (Koch-Light Laboratories, England) was recrystallized twice from methanol. The oxygen used was of high purity. The solvents, petroleum ether (boiling range, 60–80 °C), benzene, and chloroform were purified by standard procedures.

Characterization Techniques

The FT-IR spectrum was recorded on a Bruker Equinox 55 FT-IR spectrometer. The 200-MHz ¹H NMR spectra were recorded on a Bruker AC-F 200 FT-NMR spectrometer in CDCl₃. The chemical shifts were assigned with respect to tetramethylsilane. The ¹³C-NMR spectra were measured in the same spectrometer using CH₂Cl₂ as solvent (D₂O external lock). The molecular weight of the polyperoxides were obtained using a Waters ALC/GPC 224 instrument with tetrahydrofuran as a mobile phase at 30 °C using polystyrene as the standard.

The thermal analyses were done using a Perkin-Elmer DSC-2C differential scanning calorimeter (DSC) under nitrogen atmosphere at heating rates of 5, 10, 20, 40 and 80 °C · min⁻¹ with the samples of 1–5 mg. The thermogravimetric analysis (TGA) was accomplished on a Mettler Toledo TGA 850 instrument under nitrogen atmosphere at a heating rate of 10 °C · min⁻¹ with sample weights of 1–10 mg.

The ¹³C nuclear magnetic resonance relaxation experiments were carried out on a Bruker AMX 400 spectrometer operating at 100.6 MHz for the ¹³C nucleus. The sample temperature was regulated to ±1 K. Spin-lattice relaxation times (T_1) were measured by the standard inversion recovery (180- τ -90- T) pulse sequence, with a T of at least five times the longest T_1 of interest. The polymer solutions were not deoxygenated. The measured T_1 values are accurate to within 10%.

Computational Methods

The well-documented commercial software packages Insight II® and the semi-empirical program package Ampac/Mopac (version 6.0) from Biosym Technologies^[16] have been used to calculate the heats of formation. The Insight II® code assigns an empirical potential energy function to each atom from the central valence force field depending on the element type and the nature of the chemical bond. Further, this code has been benchmarked for numerous other molecular systems and its accuracy documented in the literature.^[16] The heats of formation (ΔH_f°) were computed using semi-empirical methods. The geometry of all the compounds were fully optimized using AM1 Hamiltonian.^[17,18]

Polymerizations

The polymeric peroxides were prepared using benzene solutions of the monomer and AIBN (0.02 mol · L⁻¹) in a Parr reactor equipped with stirrer (Parr Instrument Co., USA) and pressurized to 100 psi with oxygen. The polymerization was carried out at 50 ± 0.5 °C with mechanical stirring. Polyperoxide was separated from the reaction mixture by precipitating it with petroleum ether. They were isolated and purified

by repeated precipitation from benzene solution followed by the removal of the solvent by vacuum drying. It may be noted that vinyl polyperoxides, unlike acid polyperoxides, are quite safe to handle. Unlike simple organic peroxides like benzoyl peroxide, the vinyl polyperoxides are not shock sensitive, but they should be stored in the dark and in a refrigerator to minimize degradation.

Results and Discussion

Details regarding the initial monomer concentration, reaction time, yield, molecular weight and polydispersity index (PD-I) of polyperoxides are presented in Table 1. The polyperoxides have low molecular weight due to various chain transfer reactions occurring during oxygen copolymerization.^[19] The ¹H- and ¹³C-NMR spectra (peaks – Table 2) reveal the formation of alternating copolymer of vinyl monomer and oxygen. No homopolymer impurities could be detected from the NMR spectra.

The IR spectrum shows absorptions characteristic of the repeat units of the polymer given in Table 2. The weak broad absorption at 3450–3600 cm⁻¹ is observed due to the hydroxyl and hydroperoxide end groups. The formation of these end groups via various chain transfer mechanisms has been reported in the literature.^[20,21] The ¹H-NMR spectra show signals corresponding to methy-

Table 1. Experimental data for the oxidative polymerization initiated by AIBN at 50 °C.

Polymer	Monomer conc. × 10 ³ mol · L ⁻¹	Reaction time h	Yield wt.-%	Molecular weight	PD-I
PPMSP	1.64	48	21	5190	1.7
PPBrSP	1.64	48	26	4030	1.3
PPTBSP	1.64	60	17	5360	1.6

Table 2. Spectroscopic data of the polyperoxides.

Infrared spectra		¹ H NMR		¹³ C NMR	
Assignment	Wavenumber cm ⁻¹	Assignment	δ ppm	Assignment	δ ppm
PPMSP					
ν _{C-H}	2870–3027	—CH ₃	2.28	—CH ₃	20.88
ν _{O-O}	1030	—OCH ₂	4.02	—OCH ₂	75.67
ν _{C-O}	1107	—OCH	5.27	—OCH	82.54
		Ar—H	7.05–7.25	Ar—C	127–138.1
PPBrSP					
ν _{C-H}	2872–3048	—OCH ₂	4.03	—OCH ₂	75.4
ν _{O-O}	1010	—OCH	5.24	—OCH	82.1
ν _{C-O}	1075	Ar—H	7.08–7.40	Ar—C	122–136.5
PPTBSP					
ν _{C-H}	2867–2970	—CH ₃	1.25–1.36	—CH ₃	31.1
ν _{O-O}	1017	—OCH ₂	4.06	—C(CH ₃) ₃	34.5
ν _{C-O}	1108	—OCH	5.31	—OCH ₂	75.7
		Ar—H	7.16–7.27	—OCH	82.5
				Ar—C	125.3–151.3

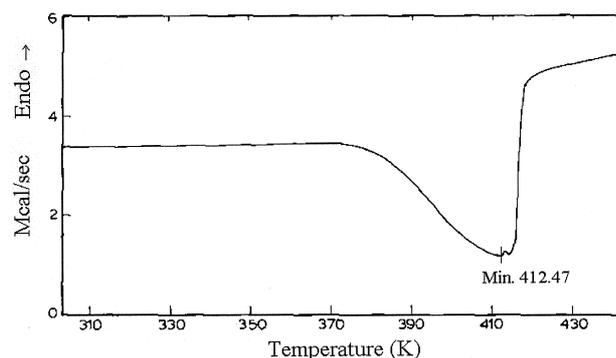


Figure 1. DSC thermogram of PPMSP at a heating rate of 10 °C · min⁻¹.

lene and methine protons shifted downfield due to two oxygen atoms directly bonded to it. For the same reason ¹³C-NMR spectra also show considerable downfield shift for the backbone carbon atoms. The polyperoxides show a very weak peak around 9.75 ppm in ¹H NMR and at 170 ppm in ¹³C NMR due to the O=CH— group present as chain ends.

For the polymers, DSC studies reveal a highly exothermic degradation. A typical DSC thermogram of PPMSP is given in Figure 1. The enthalpy of degradation, ΔH_d^0 calculated from the mean area under the exotherm at various heating rates is listed in Table 3, after applying the correction for the heat of vaporization of formaldehyde. The ΔH_v^0 for formaldehyde is reported to be 5.90 kcal · mol⁻¹.^[22] The ΔH_f^0 of the compounds studied here in their optimized structure are listed in Table 4.

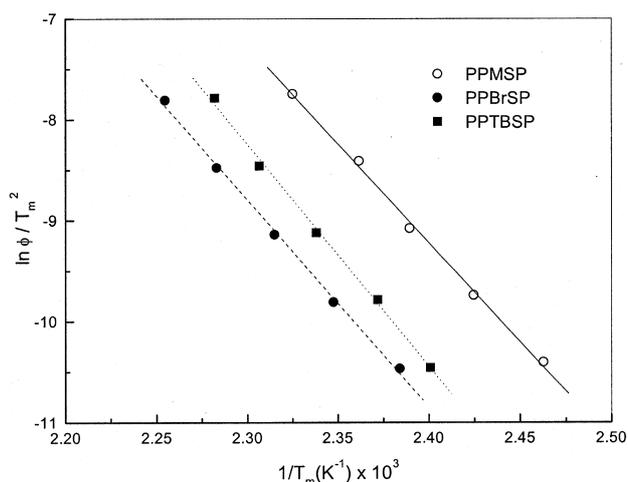
A Kissinger plot^[23] of $\ln \phi / T_m^2$ against $1/T_m$, where ϕ is the heating rate and T_m (K), the peak temperature in the DSC thermogram is given in Figure 2 for all the three polyperoxides. The slope of this plot gives the activation energy for the degradation process (E_d). The E_d values

Table 3. DSC data for the polyperoxides investigated.

Polymer	ΔH_d^0 kcal · mol ⁻¹	E_d kcal · mol ⁻¹	T_g °C
PSP	-50 ^[6]	38.2 ^[7]	-3.7
PPMSP	-49.4	39.0	4.6
PPBrSP	-50.0	-	9.6
PPTBSP	-51.3	43.7	19.9

Table 4. Thermochemical data.

Compound	Value ΔH_f^0 kcal · mol ⁻¹	Ref.
PMS	31.0	this work
PBrS	43.4	this work
PTBS	20.2	this work
Formaldehyde (g)	-27.7	[22, 24]
<i>p</i> -methylbenzaldehyde	-16.8	this work
<i>p</i> -bromobenzaldehyde	-3.5	this work
<i>p</i> -tert-butylbenzaldehyde	-27.6	this work
PPMSP	13.9	this work
PPBrSP	26.3	this work
PPTBSP	3.1	this work

Figure 2. Kissinger plot of $\ln \phi/T_m^2$ versus $1/T_m$, for PPMSP (○), PPBrSP (●) and PPTBSP (■).

were found to lie between $39\text{--}44 \pm 2$ kcal · mol⁻¹, (Table 3) which is comparable to the dissociation energy of the O—O bond, 32 kcal · mol⁻¹.^[25,26] This, as well as the symmetry of the DSC thermogram (Figure 1), suggests that the degradation of the polymers is a single-step process, which is initiated by the scission of the O—O bond. A single-step weight loss in the thermogram curve (Figure 3) supports this inference. The thermal stability of the three polyperoxides could be compared from the E_d values: the lower the E_d values, the higher is the rate of thermal degradation. On the basis of the degradation product analysis and the E_d values for the degradation process (corresponding to the cleavage of the O—O bond), a radical chain scission

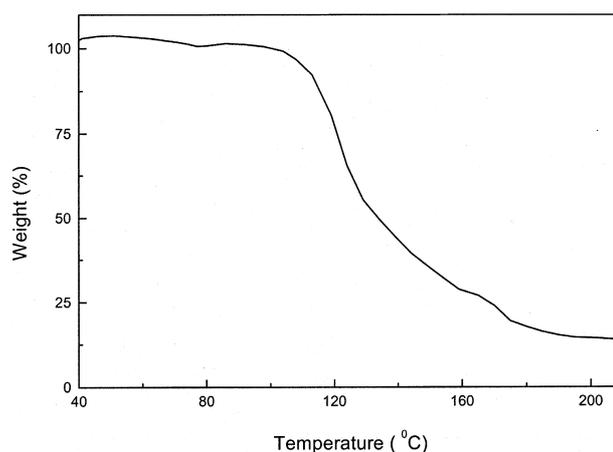
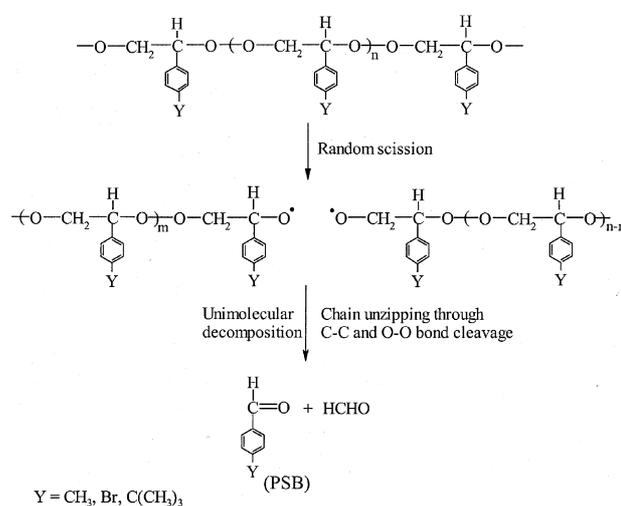


Figure 3. TGA curve of PPMSP.



Scheme 1.

mechanism, similar to that for PSP,^[27] could be proposed for the degradation (Scheme 1).

Small amounts of products other than formaldehyde and *p*-substituted benzaldehyde (PSB), could be formed via disproportionation, which is also operative in PSP.^[27] The above mechanism indicates that the exotherm observed in the DSC is due to the primary degradation of the polymer. This finds support from the thermochemical calculations.^[4]

In order to calculate the heat of degradation (ΔH_d^0), the heat of formation (ΔH_f^0) of the corresponding polyperoxide should be known. It can be evaluated from the heat of polymerization (ΔH_p^0).

Polyperoxide is formed by the reaction of O₂ with the monomer (Scheme 2).

This process involves the scission of one C=C and one O=O bond and the formation of one O—O, one C—C, and two C—O bonds. Using bond energy data from the literature,^[25,26] the calculated value of ΔH_p^0 is



Scheme 2.

20.9 kcal · mol⁻¹. However, ΔH_p^0 is also dependent upon the structural factors.^[4] For example, in vinyl polymerization, the cleavage of one C=C bond in the monomer leads to the formation of two C—C bonds in the polymer and the heat evolved in the process is 19.8 kcal · mol⁻¹, as compared to the experimental ΔH_p^0 value of 16 kcal · mol⁻¹ for poly(*p*-chlorostyrene)^[28] giving a difference of 3.8 kcal · mol⁻¹. Taking into consideration the correction due to structural factors, an average ΔH_p^0 value was taken as 17.1 kcal · mol⁻¹ for all the three polyperoxides investigated. Using this value and the ΔH_f^0 for the monomer, the ΔH_f^0 of the polyperoxides were calculated and are given in Table 4. The ΔH_d^0 for polyperoxides (PP) were calculated by two different procedures.

1) Using ΔH_f^0 , the heat change during the above degradation process was calculated using the expression $\Delta H_f^0(\text{PP}) \rightarrow \Delta H_f^0(\text{PSB}) + \Delta H_f^0(\text{CH}_2\text{O}) + \Delta H_d^0$.

It was found to be -52.5, -51.6 and -52.5 kcal · mol⁻¹ for PPMSP, PPBrSP and PPTBSP respectively, after applying correction for the heat of vaporization.

2) The value of ΔH_d^0 was calculated from the bond dissociation energies. During the process of polyperoxide degradation, one C—C and one O—O bonds are broken while two C—O bonds are converted to two C=O bonds, and formaldehyde gets vaporized. The calculated enthalpy change (ΔH_d^0) for this process is -50.3 kcal · mol⁻¹.

Based on the ΔH_d^0 values calculated by the two methods, the mean value of ΔH_d^0 of -51.4, -50.95 and -51.4 kcal · mol⁻¹ was obtained for PPMSP, PPBrSP and PPTBSP respectively. The calculated values of ΔH_d^0 for the polyperoxides suggest that the degradation process should be exothermic. The experimental ΔH_d^0 for the polyperoxide is comparable with that predicted theoretically from ΔH_f^0 and bond energies. The experimentally obtained ΔH_d^0 values are in good agreement with those calculated thermochemically, demonstrating that the proposed mechanism of degradation seems acceptable. Small differences between the experimental and theoretical values of ΔH_d^0 may arise from (a) the approximation involved in the input thermochemical data, (b) occurrence of minor side reactions during the degradation and (c) lower yields of the aldehydes under the experimental conditions.

Spin-Lattice Relaxation Time

As a representative system, normal and typical FT-NMR spectra of PPMSP are given in Figure 4. Each amplitude $A(t)$ obtained from sets of such spectra was utilized to determine T_1 according^[29] to Equation (1):

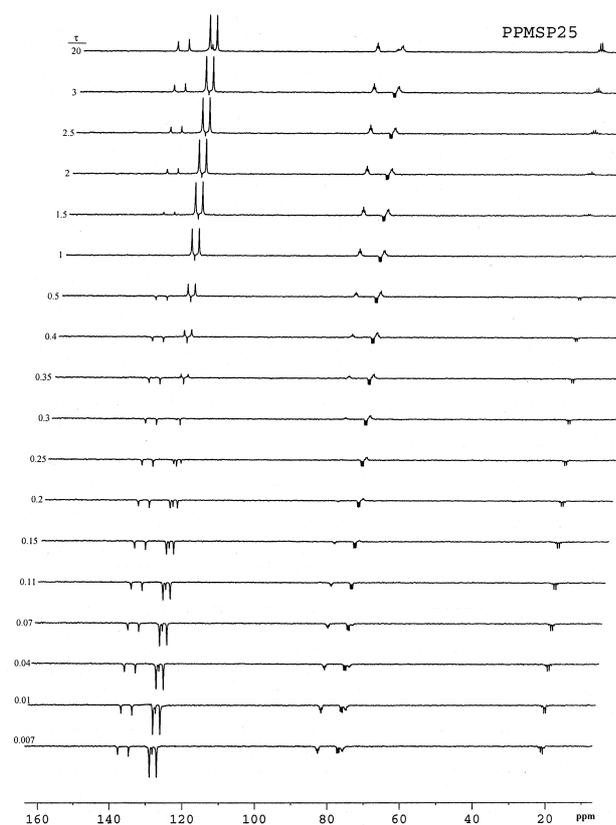


Figure 4. Proton-decoupled, natural abundance, ¹³C FT-NMR spectra of PPMSP in 20 wt.-% solution of CDCl₃ at 100.6 MHz and 25 °C.

$$A(t) = A_0 \{1 - 2 \exp(-\tau/T_1)\} \quad (1)$$

where A_0 is the equilibrium amplitude measured in a normal FT spectrum and τ is the time interval between 180° and 90° pulses. The assumption of exponential recovery in Equation (1) is justified by the good linearity in the plots of $\ln\{(A_0 - A)/2A_0\}$ versus τ . The estimated values of T_1 for 20 wt.-% solution of polyperoxides at different temperature are given in Table 5, together with those for atactic polystyrene of low molecular weight from this investigation and from that of Heatley.^[30] The 2:1 ratio of T_1 values for the α - and β -carbon atoms confirm the dipole-dipole nature of the backbone carbon relaxation. This is also true for polystyrene and can be interpreted as indicating that the chain motion is effectively isotropic.^[1]

The temperature dependence of T_1 is shown in Table 5. In order to analyze the ¹³C spin-lattice relaxation mechanism, we have assumed a purely ¹³C-¹H dipole-dipole interaction. The spin-lattice relaxation of a ¹³C nucleus arising from dipole-dipole interaction with bonded protons is given by:

$$\frac{1}{NT_1} = \frac{1}{10} \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{r_{C-H}^6} \chi(\tau_c) \quad (2)$$

Table 5. ^{13}C - T_1 values for the backbone carbon atoms of the polyperoxides in 20 wt.-% solution in CDCl_3 .

Polyperoxide	Temp. K	T_1 s \pm 10%	
		CH_2	CH
PSP ^{a)}	306	0.055	0.100
PSP	298	0.156	0.310
PPMSP	298	0.147	0.294
	288	0.107	0.216
	278	0.081	0.165
PPBrSP	298	0.136	0.273
	288	0.097	0.193
	278	0.067	0.143
PPTBSP	298	0.134	0.268
	288	0.095	0.190
	278	0.064	0.127

^{a)} Solvent CHCl_3 , Molecular weight = 4000, Conc. 22 wt.-%.

where,

$$\chi(\tau_c) = \frac{\tau_c}{1 + (\omega_H - \omega_C)^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_C^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2 \tau_c^2} \quad (3)$$

Here, τ_c is the single correlation time expressing an exponential decay of the motional autocorrelation function and prescribing the frequency spectrum of the motion concerned; γ_C and γ_H are the magnetogyric ratios and ω_H and ω_C are the resonant frequencies for ^{13}C and ^1H , respectively; $r_{\text{C-H}}$ is the C-H bond length (taken here as 1.10 Å) and N is the number of directly bonded protons.

In the “extreme-narrowing limit”, when $\omega_C \tau_c \ll 1$, Equation (2) simplifies to^[31]

$$\frac{1}{NT_1} = \frac{1}{10} \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{r_{\text{C-H}}^6} \tau_c = 2.03 \times 10^{10} \tau_c \quad (4)$$

For small molecules, with tumbling times of the order of picoseconds, Equation (4) holds good for dipole-dipole interactions, but other mechanisms of relaxation, principally spin rotation and chemical shift anisotropy may contribute substantially.^[32] For polymers, the situation is rather different, owing to their relatively slow motions and rapid nuclear relaxation. For carbon atoms with directly bonded proton or protons, only the dipolar interactions with these protons need be considered. For quaternary and carbonyl carbon atoms dipole-dipole interactions with nearest-neighbor protons are normally dominant.

The marked temperature dependence of T_1 shows that the observations are on the high frequency side of the T_1 minimum. The data show that the polyperoxides are considerably more flexible than polystyrene, the main chain

Table 6. Activation energies for molecular motions determining the spin-lattice relaxation in the 20 wt.-% solution in CDCl_3 .

Polymer	E_a kJ \cdot mol ⁻¹	
	Segmental motion of the skeleton	Internal motion of the side group
PSP	18.2	25.3 (Ph)
PPMSP	19.9	28.0 (Ph)
		7.0 (Me)
PPBrSP	24.5	30.6 (Ph)
PPTBSP	25.7	31.5 (Ph)
		11.4 (Me)

T_1 values being almost twice as long under comparable conditions. Hence it is clear that the higher the T_1 values, the more flexible the backbone.^[1] Notably the T_1 values of the backbone carbon atoms as well as the side chain carbon atoms also follow this behavior, that is T_1 increases with increasing temperature. The higher value of T_1 corresponds to a short correlation time τ_c , which means that the molecular motion is rapid and the molecules have only a short memory of their previous state of motion. A good basis for comparison is ^{13}C - T_1 values for backbone CH and CH_2 groups, since the C-H bond length is constant and the studies have been made under identical conditions of solvent, temperature, concentration, operating frequency, and so on.

Under “extreme-narrowing” conditions, the single correlation time motional model gives an adequate description of the chain dynamics.^[33] Accordingly, we utilize the isotropic, single- τ_c motional model, considering two types of local motions: backbone segmental reorientation and internal motion when,^[34, 35]

$$\tau_c^{-1} = \tau_R^{-1} + \tau_I^{-1} \quad (5)$$

Here τ_R is the correlation time for the isotropic skeletal reorientation and τ_I for internal rotation of the group attached to a skeleton undergoing isotropic motion.

From the temperature dependence of the correlation time, we can estimate the activation energy E_a for the motions determining spin-lattice relaxation using the relation^[36]

$$\tau = \tau_0 e^{E_a/RT} \quad (6)$$

where τ_0 is the correlation time expected at infinite temperature. The activation energies for the polyperoxides estimated from the plot of $\ln \tau$ versus $1/T$ are given in Table 6.

The activation energy for the skeletal motion of the polyperoxides is different, showing that the side chains impede chain mobility and that the larger the side chain the slower the motion, and also the higher the activation energy, which could be attributed to steric hindrance by the larger side chain spacers. On the basis of T_1 values

and the calculated activation energies, it was found that the flexibility follows the order PSP > PPMSP > PPBrSP > PPTBSP > PS. The small non-polar methyl group in the *para*-position has very little effect on the backbone mobility since the methyl group undergoes free rotation. This has been observed in the case of polystyrene derivatives with a methyl group at *meta* and *para* positions.^[37]

Glass transition temperatures (T_g) for the polyperoxides under nitrogen atmosphere at a heating rate $10^\circ\text{C} \cdot \text{min}^{-1}$ are given in Table 3. Interestingly the order of mobility deduced from T_1 values and the calculated activation energies roughly follow the order of glass transition temperature of the bulk polymers, showing that motions in solution and in the bulk glass appear to be closely related. The glass transition arises from the onset of backbone motions similar to, but perhaps of larger scale than, those determining magnetic relaxation in solution.^[38] Inter-chain interactions and entanglements prevalent in the solid of course greatly diminish the rate of these processes, but the frequencies are scaled proportionately.

Conclusions

The 1:1 copolymeric structure of all the three polymeric peroxides was confirmed spectroscopically for the first time. A radical chain-scission mechanism for the degradation has been proposed on the basis of the degradation products and kinetic studies. Further, as in PSP, all these polymers show a highly exothermic heat of degradation. Evidently these polyperoxides should also show auto-pyrolizability and auto-combustibility, though no such studies have been carried out.

On the basis of activation energies for the overall tumbling and segmental motions and the T_g values, it was found that flexibility follows the order PSP > PPMSP > PPBrSP > PPTBSP > PS, that is the polyperoxide chain is more flexible than that of the hydrocarbon backbone analogue. These findings are consistent with the known low rotational barriers at the heteroatoms.^[39]

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