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Synthesis, structural characterization, thermal studies and chain dynamics of poly(methacrylonitrile peroxide) by NMR spectroscopy

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Abstract

Poly(methacrylonitrile peroxide) (PMNP) has been synthesized from methacrylonitrile by free radical initiated oxidative polymerization and characterized by different spectroscopic methods. NMR spectroscopy confirmed the alternating copolymer structure with labile peroxy bonds in the main chain. The extreme instability of PMNP was noted from FTIR spectroscopy. Thermal degradation studies by using differential scanning calorimetry and thermogravimetry have revealed that PMNP degrades highly exothermically and the heat of degradation, 42.5 kcal mol^{-1}, is of the same order as that reported for other vinyl polyperoxides. Mass spectral fragmentation pattern under electron impact (EI) condition has also been investigated. The mechanism of the primary exothermic degradation has been substantiated by thermochemical calculations. The chain dynamics of the polyperoxide chain has been studied by means of ^{13}C spin–lattice relaxation times (T_1) of the main chain as well as the side chain carbons. The temperature dependence of the spin–lattice relaxation times shows that the PMNP is more flexible compared to the analogous poly(styrene peroxide). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(methacrylonitrile peroxide); Exothermic thermal degradation; Chain dynamics

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1. Introduction

In view of some significant explorations on their physicochemical properties, the vinyl polyperoxides, which are a narrow but important class of polymers, are witnessing a renaissance. Recent reports point to the potential of polymeric peroxides as specialized thermal [1,2] and photo-initiators [3] to synthesize homopolymers and block copolymers from vinyl monomers. Their technological importance as fuels [4] and curators in coating and molding applications [5] has also been established and it emphasizes the need to synthesize such new materials. Since the first report in 1925 by Staudinger and Schwalbach [6], only a small number of polyperoxides have been investigated, and most of the earlier works dealt with the mechanism and kinetics of the oxidative polymerization of various vinyl monomers [7]. The spectral characterization of polyperoxides was initiated by Cais and Bovey [8] in 1977. However, only a few polyperoxides have been spectroscopically characterized [9]. Of these, poly(styrene peroxide) (PSP), first reported by Bovey and Kolthoff [10], has received considerable attention. Recently, PSP has been shown to behave as a unique auto-combustible polymer fuel, its combustion being controlled by degradation [4]. Poly(methacrylonitrile peroxide) (PMNP), another member of this class of polymers was reported along with its degradation product by Strause and Dyre [11], but its spectral characterization has not been made.

The principal features of interest in these polyperoxide systems are the effect of heteroatom unit on the transmission of configurational information, as detected by NMR, and the chain dynamics behavior, particularly in relation to the hydrocarbon-backbone analogs [12,13]. The heteroatom units in the main chain are expected to impart a wide range of flexibilities to the backbone [14]. Also the carbon atoms of the side chain, allow one to monitor the reorientation of these side groups, which in turn is dependent on the steric influence of the heteroatom unit.

In view of the resurgence of polyperoxides as technologically important materials, we present here the synthesis and spectral characterization of PMNP. The ^{1}H and ^{13}C NMR spectra and thermal degradation of PMNP have been studied. Results of the investigations on the spin–lattice relaxation of the different backbone carbons of the polyperoxide, which leads to an understanding of the mobility of the polymer unit are also discussed.

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2. Experimental

2.1. Materials

Methacrylonitrile (MN) (Lancaster, UK) was used as received. Azobis(isobutyronitrile) (AIBN) (Koch Light Laboratories, UK) was recrystallized three times before use. Oxygen of high purity was used. Commercial petroleum ether, chloroform, etc., were purified before use.

2.2. Methods

The FTIR spectrum was recorded on a Bruker Equinox 55 FTIR spectrometer. The 200 MHz ^{1}H NMR spectra were recorded on a Bruker AC F 200 FT NMR spectrometer in $CDCl_3$. The chemical shifts were assigned with respect to tetramethylsilane (TMS). The ^{13}C NMR spectra were recorded in the same spectrometer using CH_2Cl_2 as a solvent. The molecular weight of the polyperoxide was obtained using a Waters ALC/GPC 224 instrument with THF as a mobile phase at 30°C using polystyrene as standard.

The thermal analysis was carried out using a Perkin–Elmer DSC-2C differential scanning calorimeter at heating rates of 5, 10, 20, 40 and 80°C min^{-1} with sample sizes of 1–5 mg. The thermogravimetric analysis (TGA) was accomplished on a Mettler Toledo TGA 850 instrument at a heating rate of 10°C min^{-1} with a sample weight of 23.93 mg. Electron impact mass spectra (EI-MS) in the positive mode were obtained at 70 eV in JEOL JMX-DX-303-GC mass spectrometer. The samples were introduced by direct inlet probe and were heated from 25 to 400°C at a heating rate of 64°C min^{-1}.

The ^{13}C NMR relaxation experiments were carried out on a Bruker AMX 400 spectrometer operating at 100.6 MHz for the ^{13}C nucleus. Spin–lattice relaxation times were measured by the standard inversion recovery ($180-\tau-90-T$) pulse sequence, with a T of at least five times the longest T_1 of interest. The polymer solutions were not deoxygenated. All chemical shifts are referenced to internal TMS. The sample temperature was regulated to ±1 K. The measured T_1 values are accurate to within ±10%.

2.3. Computational methods

The well-documented commercial software packages Insight II® and the semiempirical program package AMPAC/MOPAC (version 6.0) from Biosym Technologies [15] was used. The MSI Insight II® code assigns an empirical potential energy function to each atom from the central valence force field (cvff) 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. The geometries of all the compounds were fully optimized using AM1 Hamiltonian [16,17].

2.4. Polymerization

MN was oxidatively polymerized by charging a solution of MN and AIBN (0.02 mol l^{-1}) in a Parr reactor equipped with a stirrer (Parr Instrument, USA), thermostated at 50 ± 0.5°C for 30 h under oxygen pressure of 150 psi using the procedure described elsewhere [5]. PMNP was separated from the reaction mixture by precipitating it with petroleum ether and purified by repeated precipitation followed by the removal of solvent by vacuum drying. The yield of PMNP was found to be 19%. Micro-analysis of PMNP was carried out using Carlo Erba elemental analyzer Model 1106 at the Department of Organic Chemistry of the Institute. The experimental values are C, 49.63%; H, 5.46%; N, 13.62% in agreement with the calculated values of C, 48.48%; H, 5.05%; N, 14.14% for $C_4H_5NO_2$.

3. Results and discussion

3.1. Molecular weight

PMNP was separated as a yellowish viscous liquid. The number average ($\bar{M}_n$) and weight average ($\bar{M}_w$) molecular weights of PMNP were found to be 2190 and 3670, respectively. The rather low molecular weight of PMNP is very similar to that of the other vinyl polyperoxides ($\bar{M}_n =$ 300–5000) [18]. A detailed examination of the mechanism of formation revealed that this category of polymers undergo facile degradation during oxygen copolymerization itself, generating chain transfer agents such as aldehydes, which react with macro growing radical, resulting in low molecular weight.

3.2. ^{1}H NMR spectra

The ^{1}H NMR spectrum of PMNP is shown in Fig. 1. No homopolymer impurities could be detected from NMR spectra. All the groups present simple first-order spectra. The methyl and methylene protons constitute A_3 and A_2 spin systems, respectively [19]. The signals at δ 1.7 and

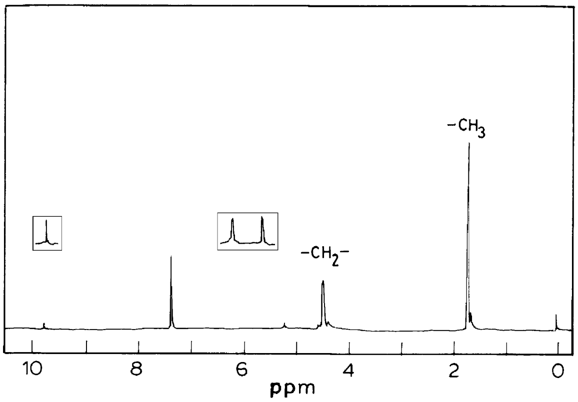


Fig. 1. ^{1}H NMR spectrum of PMNP in $CDCl_3$. Inset: peaks at 9.80 and 5.76 ppm are expanded 5 and 10 times, respectively.

4.48 ppm are assigned to the methyl and methylene protons, respectively. The methylene signal is shifted downfield due to the two oxygen atoms directly bonded to it. The methylene region shows some complexity, which could be due to the excess methylene groups present in the polyperoxide chain as defects. This is because during the oxidation of MN, the peroxy radical undergoes preferably a cleavage reaction rather than an addition reaction with MN [20]. As in the case of other vinyl polyperoxides, here too the molecular weight and the end groups are determined by the chain transfer reactions. In PMNP, as in poly(α-methylstyrene peroxide) [21], the chain begins with HO_2–CH_2–C(CH_3)(CN)– and O=CH–C(CH_3)(CN)– groups and ends with –CH=C(CH_3)(CN) group. Thus, the major terminating group in PMNP is apparently the unsaturated chain end. This is noted from the ^{1}H NMR spectrum of PMNP. The peak at δ 5.76 ppm (doublet) corresponds to the –O_2–CH^*=C(CH_3)(CN) proton and the peak at δ 9.8 ppm to the O=CH^*–C(CH_3)(CN)– proton.

3.3. ^{13}C NMR spectra

The ^{13}C NMR spectrum (Fig. 2) shows signals corresponding to the four C atoms present in the repeat unit. The signals at δ 20.5, 76.7, 78.1 and 117.5 ppm are assigned to methyl, methylene, quaternary carbon and CN group, respectively. Considerable downfield shift for the backbone carbons are due to the two electronegative oxygen atoms bonded to it. A very small peak at 168.57 ppm is assigned as the carbonyl group present at the chain end. The signal corresponding to the unsaturated carbon of the terminating group appears in the region of aromatic carbons at 128.3 ppm [22]. The very low intensity peak at 92.74 ppm may be assigned to (–O–CH_2–O–) group in the chain. It reveals the occurrence of cleavage reactions to a considerable extent during the oxidative polymerization. The inclusion of –O–CH_2–O– in the polyperoxide chain is reported for the oxidation of α-methylstyrene [20].

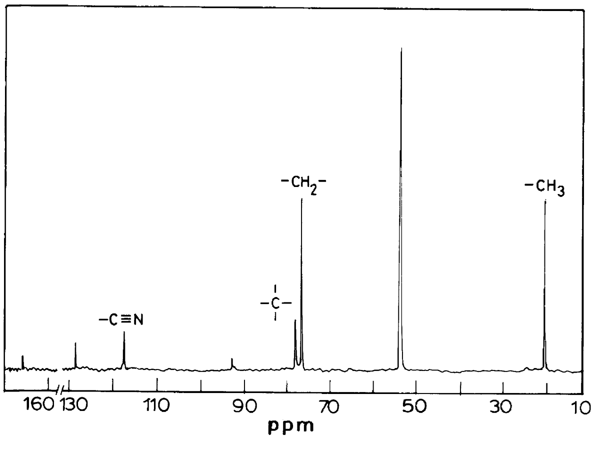


Fig. 2. ^{13}C NMR spectrum of PMNP in CH_2Cl_2 (D_2O as external lock).

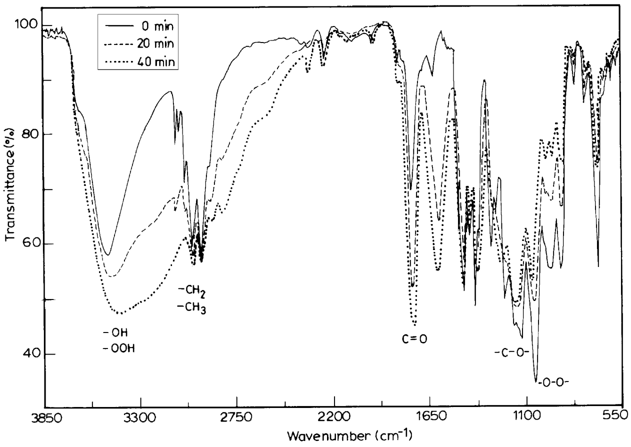


Fig. 3. FTIR spectra of PMNP recorded at different intervals of time: (I) immediately after isolation, 0 min; (II) after 20 min; (III) after 40 min of keeping the sample in the IR instrument at room temperature.

3.4. FTIR spectra

The FTIR spectra of PMNP taken at different intervals of time are shown in Fig. 3. The spectrum recorded immediately after the isolation (Fig. 3(I)) shows a strong band near 1040 cm^{-1} which is assigned to the peroxide (O–O) bond stretching, while the intense band at 1132 cm^{-1} is due to the C–O stretching. The two intense bands appearing in the region 2920–3015 cm^{-1} are assigned to the CH_3 and CH_2 stretching modes. The weak band at 2245 cm^{-1} is due to C≡N stretching and in several compounds, it usually appears as a weak band. The broad absorption centered at 3480 cm^{-1} is attributable to the hydroxyl and hydroperoxide end groups. The formation of these end groups via various chain transfer mechanism is known in the literature [23,24]. The intense band appearing at 1755 cm^{-1} is assigned to the carbonyl groups of the type O=CH–C(CH_3)(CN)–. The weak absorption at 1623 cm^{-1} is due to the stretching of C=C bond present at the chain ends.

The instability of PMNP is revealed by the FTIR spectra depicted in Fig. 3. Spectrum (I) was obtained immediately after the polyperoxide was isolated. The spectra (II) and (III) were taken after keeping the sample at room temperature for 20 and 40 min, respectively. It is seen that the peroxide stretching band at 1040 cm^{-1} gradually vanishes, concomitantly, the hydroxyl band centered at 3482 cm^{-1} broadens and the carbonyl band at 1755 cm^{-1} is intensified. Thus, PMNP undergoes decomposition forming the alkoxy radicals, formaldehyde and pyruvonitrile. The compound probably undergoes somewhat faster decomposition when exposed to infrared radiation while taking the spectrum. The degradation product formaldehyde also stabilizes the alkoxy radicals by hydrogen transfer forming the hydroxyl end groups [24].

Based on the above discussion and in agreement with the

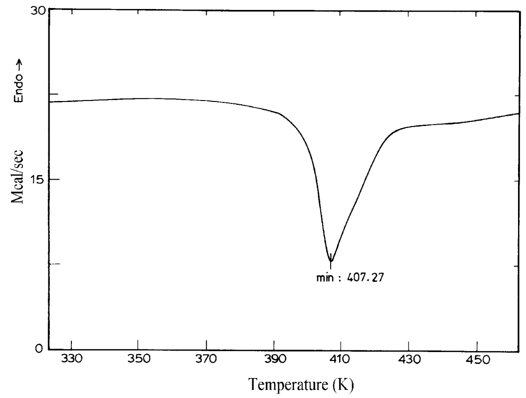
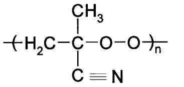


Fig. 4. DSC thermogram of PMNP at a heating rate of 10°C min^{-1}.

elemental analysis, the general formula of PMNP can be written as



$$\left[H_2C-\underset{C\equiv N}{\overset{CH_3}{C}}-O-O \right]_n$$

3.5. Thermal degradation

The DSC studies were performed at heating rates of 5, 10, 20, 40 and 80°C min^{-1}. A typical thermogram is given in Fig. 4. The DSC studies reveal that PMNP undergoes a highly exothermic and complete degradation. No residue was found in the pan after the degradation. The enthalpy of degradation, ΔH_d^0, calculated from the mean area under the exotherm at different heating rates, was found to be -42.5 ± 2 kcal mol^{-1}, after applying corrections for the heat of vaporization of pyruvonitrile and formaldehyde by using the thermochemical data given in Table 1. The heats of formation (ΔH_f^0) computed using semiempirical methods are presented in Table 1.

Kissinger's plot [25] of ln ϕ/T_m^2 against $1/T_m$, where ϕ represents the heating rate and T_m, the peak temperature in the DSC thermogram, is given in Fig. 5. The slope of this plot provides the activation energy (E_d) for the degradation process. The value of E_d was found to be 36.38 ± 2 kcal mol^{-1}, which is comparable with the dissociation energy of the O–O bond (Table 2). This value, as well as the symmetry of the DSC thermogram (Fig. 4), suggests that the degradation of PMNP is a single-step process, initiated by the scission of the O–O bond. The TGA (Fig. 6) of the polymer was carried out at a heating rate of 10°C min^{-1}. The weight loss occurs in a single step sharply around 120°C.

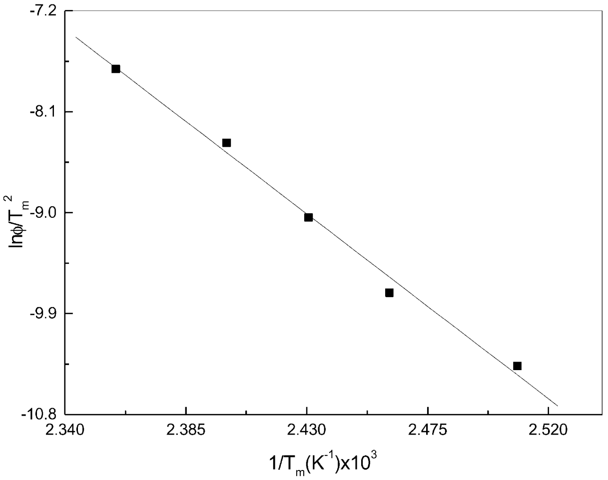
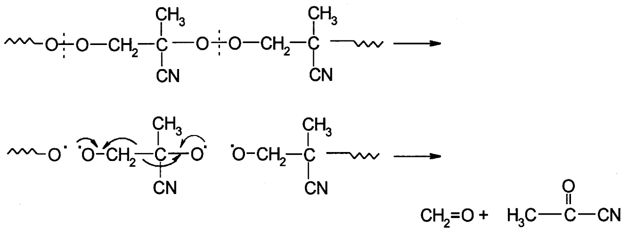


Fig. 5. Kissinger's plot of ln ϕ/T_m^2 against $1/T_m$.

On the basis of the degradation product analysis [11] and the measurement of E_d for the degradation process (which corresponds to the cleavage of the O–O bond), a radical chain scission mechanism, similar to that reported for PSP [26], could be given for the degradation of PMNP as shown below.



Small amounts of other products may be formed, via disproportionation reaction, as in the degradation of PSP [26]. The above mechanism indicates that the exotherm observed in the DSC is due to the primary degradation of PMNP. It is supported by the thermochemical calculations, discussed below.

Table 1
Thermochemical data

Compound	ΔH_f^0 (kcal mol^{-1})		ΔH_v^0 (kcal mol^{-1})	
	Value	Reference	Value	Reference
MN	37.8	This work		
Pyruvonitrile (l)	− 5.0	This work	11.81[a]	This work
Formaldehyde (g)	− 27.7	[29,30]	5.9	[29]
PMNP	23.2	This work		

[a] Calculated by group additivity method [31,32].

Table 2
Bond energy data

Bond type	Bond energy (kcal mol^{-1})	Reference
C=C	145.8	[33,34]
C–C	82.8	[34]
C=O formaldehyde	166.0	[33,34]
C=O ketones	179.0	[33,34]
C–O	85.5	[33,34]
O=O	119.1	[33,34]
O–O	32.0	[34]

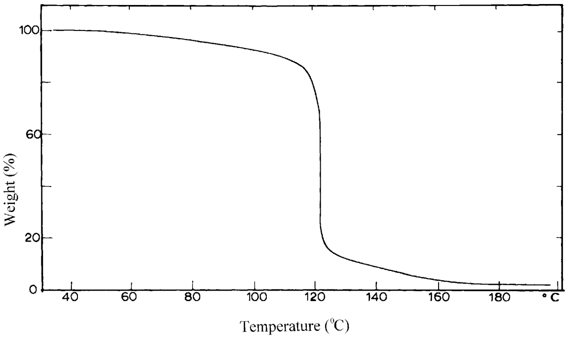


Fig. 6. TGA curve of PMNP at a heating rate of 10°C min^{-1}.

In order to calculate the heat of degradation (ΔH_d^0), the heat of formation (ΔH_f^0) of PMNP is required. It was evaluated from the heat of polymerization (ΔH_p^0).

The PMNP is obtained by reacting O_2 with MN,

$$n\mathrm{CH_2{=}C(CH_3)(CN)} + n\mathrm{O_2}$$

$$\rightarrow \mathrm{-[-O{-}CH_2{-}C(CH_3)(CN){-}O{-}]_n-} + \Delta H_p^0$$

In this process, one C=C and one O=O bond are broken to form one O–O, one C–C, and two C–O bonds. Using the bond energy data of Table 2, the value of ΔH_p^0 for PMNP was calculated to be 20.9 kcal mol^{-1}. However, ΔH_p^0 is also dependent upon structural factors. For example, in vinyl polymerization, the breakage of one C=C bond gives rise to two C–C bonds and the heat evolved in the process is 19.8 kcal mol^{-1}, as compared to the experimental value of ΔH_p^0, 13.5 kcal mol^{-1}, for polymethacrylonitrile (PMN) [27], giving a difference of 6.3 kcal mol^{-1}. Taking into consideration the dependence on structural factor [28], we have therefore taken the actual value of ΔH_p^0 PMNP as 14.6 kcal mol^{-1}. Using this value and the ΔH_f^0 for MN, the calculated ΔH_f^0 of PMNP is 23.2 kcal mol^{-1}.

The value of ΔH_d^0 for PMNP was calculated by two different procedures:

1. Using ΔH_f^0, we can theoretically calculate the heat change during the degradation from the above degradation scheme,

   $$\Delta H_f^0(\mathrm{PMNP})$$

   $$\rightarrow \Delta H_f^0(\mathrm{CH_3{-}CO{-}CN}) + \Delta H_f^0(\mathrm{CH_2{=}O}) + \Delta H_d^0$$

   It was found to be −38.19 kcal mol^{-1} after applying the corrections for the heat of vaporization of the products using the data given in Table 1.
2. The value of ΔH_d^0 was calculated from the bond dissociation energies. During the process of degradation of PMNP, a C–C and a O–O bonds are broken while two C–O bonds are converted into two C=O bonds, and pyruvonitrile and formaldehyde are vaporized. The calculated enthalpy change (ΔH_d^0) for this process is −41.49 kcal mol^{-1}.

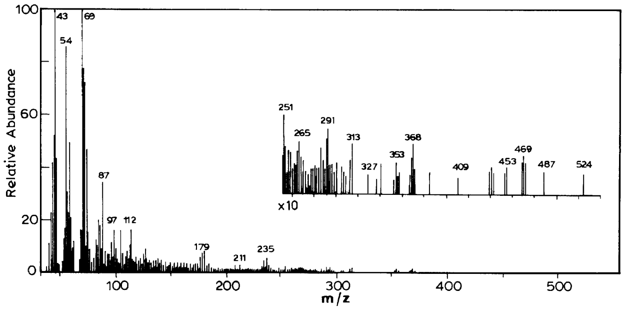


Fig. 7. EI-MS spectrum of PMNP.

Based on the values obtained by the above two methods (−38.19 and −41.49 kcal mol^{-1}), a mean value of −39.84 kcal mol^{-1} was taken for ΔH_d^0 for PMNP. The calculated value of ΔH_d^0 for PMNP suggests that the process should be exothermic in nature. The experimentally measured ΔH_d^0 values are in good agreement with the thermodynamically calculated values demonstrating the acceptability of the proposed mechanism of degradation. The small discrepancy between the experimental and theoretical value of ΔH_d^0 may arise from (a) the approximation involved in the input thermochemical data, (b) occurrence of minor side reactions during degradation and (c) lower yields of the aldehydes under the experimental conditions.

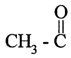
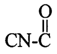
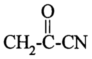
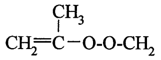
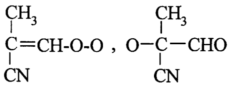
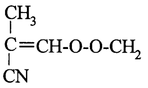
3.6. Mass spectra

The EI-MS spectrum of PMNP is presented in Fig. 7. The EI-MS technique is suitable for the study of the primary degradation products of polymers since the pyrolysis is carried out close to the ion chamber under high vacuum. The primary pyrolysis products formed are rapidly removed from the hot zone and detected immediately. The base peak at $m/z = 69$ in the spectrum corresponds to the H_3C–CO–CN. The assignment of the molecular ion peaks found in the spectra is given in Table 3.

3.7. Chain dynamics

The measurement of nuclear relaxation furnishes a powerful means of studying the dynamics of macromolecules. In solution measurements, the intramolecular influences are revealed rather than the effect of neighboring chains. The only significant mechanism for the spin–lattice relaxation of ^{1}H and ^{13}C nuclei in polymers is the dipole–dipole interaction with neighboring protons, whose motions give rise to fluctuating magnetic fields [35,36]. Under the condition of 'motional narrowing', the correlation time, τ_c,

Table 3
The molecular ions identified in the EI-MS of PMNP

Structure	m/z
 $CH_3\text{-}C(=O)$	43
 $CN\text{-}C(=O)$	54
 $CH_2\text{-}C(=O)\text{-}CN$	68[a]
 $CH_2{=}C(CH_3)\text{-}O\text{-}O\text{-}CH_2$	87
 $C(CH_3)(CN){=}CH\text{-}O\text{-}O$, $O\text{-}C(CH_3)(CN)\text{-}CHO$	98[b]
 $C(CH_3)(CN){=}CH\text{-}O\text{-}O\text{-}CH_2$	112

[a] Observed as $(MH)^+$ peak.

[b] Observed as $(M-1)^+$ peak.

according to the single correlation model [36] is given by

$$\frac{1}{NT_1} = \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{r_{C\text{–}H}^6} \tau_c \tag{1}$$

where γ_H and γ_C are the gyromagnetic ratios for the ^1H and ^{13}C nuclei, $\hbar$ the Planck's constant, $r_{C\text{–}H}$ the internuclear distance and N the number of protons attached to the carbon having spin–lattice relaxation time, T_1.

The motion of flexible polymers in solution may be conventionally regarded as being composed of segmental motion and overall tumbling. Synthetic polymers generally enjoy considerable segmental freedom in solution. When τ_c is on the fast-motion side of the T_1 minimum, T_1 increases with increasing temperature. The presence of side chains generally impedes the chain mobility, the larger the side chain, the slower is the motion. For example, the methyl group decreases the chain motion by a factor of 2–3, and the phenyl groups have a further impeding effect [36]. However, the presence of two α-substituents do not impede the chain motion significantly more than a single substituent, which may be attributed to the two substituents increasingly crowding all the rotational states, without necessarily increasing the barrier between them. However, the presence of heteroatom in the backbone increases the flexibility of the polymer chain. The effects of the heteroatoms on the chain dynamics have been discussed by Bovey and Jelinski [37].

Table 4
T_1 values for different carbons in $CDCl_3$ (20%, w/w) at different temperatures

Temperature (K)	T_1 (s) ± 10%			
	CH_3	CH_2	C_α	CN
PMNP				
298	0.519	0.231	5.194	1.119
288	0.440	0.202	4.589	0.867
278	0.375	0.173	4.030	0.678
PSP [38]				
298		0.156	0.312	
288		0.125	0.249	
278		0.092	0.184	

The T_1 values determined at 25°C for all the observable carbons are compared with those of PSP in Table 4. The marked temperature dependence of T_1 shows that the observations are on the high frequency side of the T_1 minimum, as observed also in the case of PSP [38]. The higher value of T_1 corresponds to a short correlation time τ_c, indicating that the molecular motion is rapid and the molecules have only a short memory of their previous state of motion. The main chain T_1 data show that PMNP is more flexible than PSP. The aliphatic quaternary carbon in the main chain has a T_1 value different from that of the CN-carbon, showing that they do not share motion in common [39,40].

An estimate of the methyl group rotational time in relation to the chain segmental motion and overall tumbling has been made and the results are presented in Table 5. The activation energy for the internal rotation of the methyl group was determined by assuming an Arrhenius type of activation process [41,42]. The average correlation time at each temperature can be calculated assuming an isotropic reorientation, which is based on the assumption of extreme narrowing.

The total average methyl correlation times τ_{obs} are related to the correlation times of the methyl group internal rotation and segmental motion [43] by

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_{int.\ rot}} + \frac{1}{\tau_{seg.\ motion}} \tag{2}$$

Table 5
Correlation times (ns) for chain segmental motion and tumbling (τ_c (segmental)) and methyl group rotation (τ_c (Me)), for 20% (w/w) solution of PMNP in $CDCl_3$

Temperature (K)	τ_c (segmental)	τ_c (Me)
298	0.1066	0.0449
288	0.1218	0.0537
278	0.1422	0.0631

The correlation times for internal rotation were calculated at each temperature using methylene T_1s as a measure of $\tau_{\text{segmental}}$. From the temperature dependence of the correlation times, the activation energy for the overall tumbling motion was calculated to be 9.94 kJ mol^{-1} which is much less than that reported for PSP [38]. The PMNP polymer chains enjoy more flexibility than PSP, as revealed by the lower value of the activation energy for the overall tumbling motion. The activation energy for the methyl group rotation is 11.73 kJ mol^{-1}. This is consistent with that reported (10–20 kJ mol^{-1}) for polypropylene and polyisobutylene in *o*-dichlorobenzene [44]. The error in the calculated activation energy was estimated to be less than 5%. It is interesting to note that the order of mobility is paralleled by the order of glass transition temperatures (T_g) of the bulk polymers. The T_g values for PMNP and PSP are -32.93 and -3.74°C, respectively, whereas PMN has a T_g of 120°C [45]. The lower T_g of PMNP indicates that incorporation of the peroxy bond into the main chain makes PMNP more flexible than PMN. This is also true for PSP and polystyrene [8].

4. Conclusions

The 1:1 copolymeric structure of PMNP has been elucidated spectroscopically for the first time. A radical chain-scission mechanism for the degradation of PMNP has been proposed from the analysis of its degradation products and kinetic studies. Further, PMNP also shows a highly exothermic heat of degradation similar to PSP. Because of these similarities in the degradation pattern, PMNP is also likely to shows auto-pyrolyzability and auto-combustibility, though no studies have been made. The studies reveal that the PMNP chain is more flexible than that of PSP.

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