Synthesis and Properties of a Novel (Main-Chain)–(Side-Chain) Polymeric Peroxide

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ABSTRACT: A novel (main-chain)-(side-chain) vinyl polyperoxide, poly(dipentene peroxide) (PDP), an alternating copolymer of dipentene (DP) and oxygen, has been synthesized by thermal oxidative polymerization of DP. The PDP was characterized by ^{1}H NMR, ^{13}C NMR, FTIR, DSC, TGA, and EI-MS studies. The overall activation energies of the degradation from Kissinger's method were 28 and 33 kcal/mol, respectively, for the endocyclic and acyclic peroxide units. The side-chain peroxy groups were found to be thermally more stable than the main chain. Above 45°C the rate of polymerization increases sharply at a particular instant showing an "autoacceleration" with the formation of knee point. The kinetics of autoacceleration has been studied at various temperatures (45–70°C) and pressures (50–250 psi). © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1549–1555, 2001

Key words: polyperoxide; (main-chain)-(side-chain); autoacceleration

INTRODUCTION

Compared to low molecular weight peroxides, the polymeric peroxide initiators have been found to significantly influence both the molecular weight and the molecular weight distribution of the resulting polymers. In addition, they can produce block copolymers, comb-like polymers, interpenetrating polymer networks, etc.[1,2] Vinyl polyperoxides,[3,4] which are alternating copolymers of vinyl monomers and oxygen, are of current interest due to special features such as the highly exothermic nature of their degradation,[5] the unusual phenomenon of autopyrolysis,[6] their role in explaining the paradoxical effects of oxygen in vinyl polymerization,[7] and their use in developing special fuels.[8] They have also been investigated for their role as initiators.[9,10]

Ordinarily, the rate of polymerization increases with the increases in the concentration of

an initiator, but the molecular weight decreases. This undesirable effect can be overcome by employing nontraditional initiators such as polyfunctional initiators.[1] Use of acid polyperoxides as initiators leads to not only an increase in the molecular weight with conversion but also a narrowing of molecular weight distribution.[11] Among acid polyperoxides, those with peroxide groups of varying thermal stability were found to be more suitable for this purpose.[1,2] Vinyl polyperoxides, except for poly(butadine peroxide),[12] being significantly less hazardous, are preferred over acid polyperoxides. Hence, vinyl polyperoxides, having peroxide groups of different thermal stabilities, could be more attractive as initiators than the corresponding acid polyperoxides; however, they do not show much difference in the stability of peroxy linkages.[13] It was, therefore, decided to introduce the peroxy groups both in the main chain and side chain by differing substantially in thermal stability.

We present here the synthesis and characterization of poly(dipentene peroxide), in the absence and presence of an initiator, containing peroxy

linkages both in the main chain and side chain with different thermal stabilities. The kinetics of an unconventional autoacceleration phenomenon in the thermo oxidative polymerization of dipentene has also been presented.

EXPERIMANTAL

Materials

Dipentene (Eastman Organic Chemicals, NY) was freed from the inhibitor and distilled under reduced pressure. Azobis(isobutyronitrile) (AIBN) (Koch Light Laboratories, England) was recrystallized thrice from methanol. Chlorobenzene, methanol, and petroleum ether were distilled before use.

Measurements

Dipentene (25 mL) was oxidatively polymerized in the absence and presence of an added initiator (AIBN) in a Parr reactor (Parr Instrument Company) equipped with a digital pressure transducer, temperature controller, and mechanical stirrer, at 50°C and in the pressure range of 50–250 psi, as described elsewhere. The polymerization was carried out in bulk. Only for studying the monomer variation chlorobenzene was used as a solvent. The polymerization was kept for 3 h to effect low conversion for reliable kinetic analysis. The rates were reproducible to within 5% error. After completion of the reaction, the poly(dipentene peroxide) (PDP) was precipitated in petroleum ether. The 200 MHz ^{1}H NMR spectra were recorded on a Bruker AC-F 200FT NMR spectrometer in CDCl$_3$. The chemical shifts were obtained in ppm with reference to tetramethylsilane. The FTIR spectra were recorded on a Bio-Rad FTS 7 FTIR spectrometer. Dynamic differential scanning calorimetric (DSC) experiments were carried out on a Dupont instrument, Model 910. Samples of 1–10 mg, placed in open aluminum pans, were heated at a rate of 2–20 K/min under nitrogen atmosphere. The temperature axis was calibrated using indium. The thermogravimetric (TG) study was carried out on a Dupont 951 thermogravimetric analyzer. Pyrolysis was carried out using different inlet probe in a JEOL mass spectrometer, heated from 50 to 400°C at a rate of 20 K/min. The electron ionization (EI) was maintained at 25 eV. The molecular weight of PDP was estimated by GPC (Waters HCL/GPC 244, with RI detector) using THF as solvent. The GPC instrument was calibrated using polystyrene as a standard.

RESULTS AND DISCUSSION

Molecular Weight and Spectral Characterization of PDP

Vinyl polyperoxides are generally prepared by oxidative polymerization of vinyl monomers in the presence of a free radical initiator like AIBN, at 50°C, under high pressure. Interestingly, dipentene (DP) also undergoes thermo-oxidative polymerization at 40°C with the formation of a viscous poly(dipentene peroxide) (PDP). PDP is a yellow viscous solid, soluble in common organic solvents. The molecular weight of the PDP is found to be low ($\bar{M}_n = 2390$, $\bar{M}_w = 5570$ and $\bar{M}_z = 12,390$) due to various chain transfer reactions and partial decomposition of PDP during the polymerization. Generally, vinyl polyperoxides have low molecular weight[3,4] ($\bar{M}_n = 300$–5000) due to various chain transfer reactions occurring during polymerization. Spectral analysis of the PDP shows that among the two double bonds of DP, the acyclic double bond is much less reactive than the endocyclic double bond. The main chain of the PDP is mostly formed from the oxidation of endocyclic double bonds. The various spectral assignments of PDP are given below.

FTIR (KBr): 1670 cm^{-1} for $>$C$=$CH$_2$ group, 1714 cm^{-1} for $>$C$=$O group, 1000 cm^{-1} for O—O and 3400 cm^{-1} for OH and OOH groups.

^{1}H-NMR, CDCl$_3$, TMS, δ (ppm): 0.9–2.8 for CH$_2$ and CH$_3$; 4.73 for $>$C$=$CH$_2$; 4.35 for OOCH$_2$ and 5.08 (s) for OOCH$<$.

^{13}C-NMR, CDCl$_3$, TMS: $\delta = 15$–39 ppm for $>$CH$_2$ and —CH$_3$, $\delta = 80$–85 ppm for $>$CHOO— and —CH$_2$OO—, $\delta = 200.7$ ppm for $>$C$=$O and $\delta = 120$–130 ppm for $>$C$=$CH$_2$.

{^{1}H-NMR of DP, CDCl$_3$, TMS, δ (ppm): 0.9–2.5 (m) for CH$_2$ and CH$_3$; 4.73 (s) for $>$C$=$CH$_2$ (acyclic) and 5.4 (s) for —CH$=$C$<$ (endocyclic).}

Thermal Analysis of PDP

The DSC and TG thermograms are shown in Figures 1 and 2. Unlike other vinyl polyperoxides,[14,15] which exhibit a smooth DSC trace or simple one-step TG weight-loss curve, PDP shows complex pattern indicating that the degradation process is not a single-step degradation process.
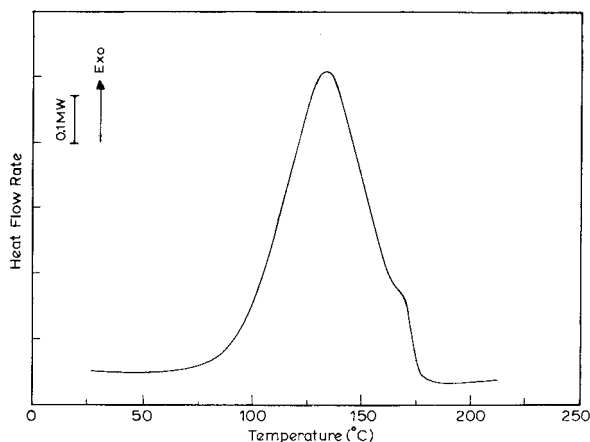
Figure 1   DSC traces of PDP.

Figure 3   EI-MS of PDP.

mograms, which show a two-step degradation (Fig. 2).

EI-MS Analysis of PDP Degradation

EI-MS of PDP, recorded at 25 eV, is shown in Figure 3. The structural assignments of EI-MS are given in Table I. The mechanism of degradation is a random chain scission of the backbone O—O bond. The product analysis shows that the major degradation products are the result of the oxidation of the ring double bond. The acyclic double bond is found to be partially oxidized. The primary products formed by the main chain degradation of the peroxide (a, b, and c of Scheme 1) further undergoes secondary degradation, which makes the mass spectrum complex. As an example mechanism for secondary degradation of structure (a) is given in Scheme 2. The degradation products are volatile, and hence, they are not isolated from the product.

There are two exotherms in the DSC pattern correspondingly two steps of degradation in the TG for PDP. This is attributed to the presence of two kinds of O—O groups in the polymer chain. Compared to other polyperoxides,[16] the PDP degrades highly exothermally, as shown in the DSC thermogram. The average enthalpy of degradation of PDP, at various heating rates, was found to be 400 kcal/g, which is much higher than other polyperoxides, supporting the presence of more than one peroxide linkage per repeat unit of PDP. The two exotherms at 130 and 170°C are due to the degradation of endo cyclic peroxide and the acyclic peroxide units of PDP respectively (Fig. 1). From the peak temperature (T_m), the overall activation energies of the peroxide degradation were obtained as 28 and 33 kcal/mol, respectively, for the endocyclic and acyclic peroxide units using Kissingers method.[17] The presence of two types of peroxide unit is also confirmed from the TG ther-
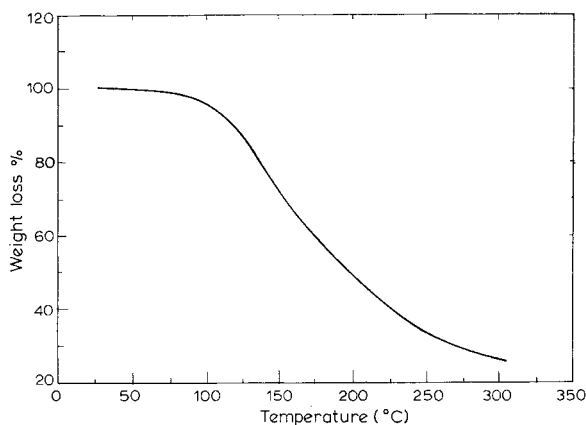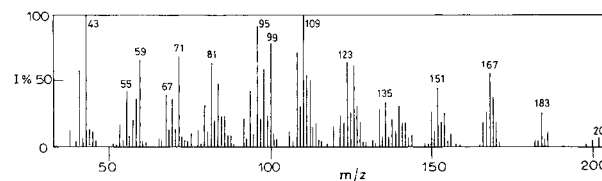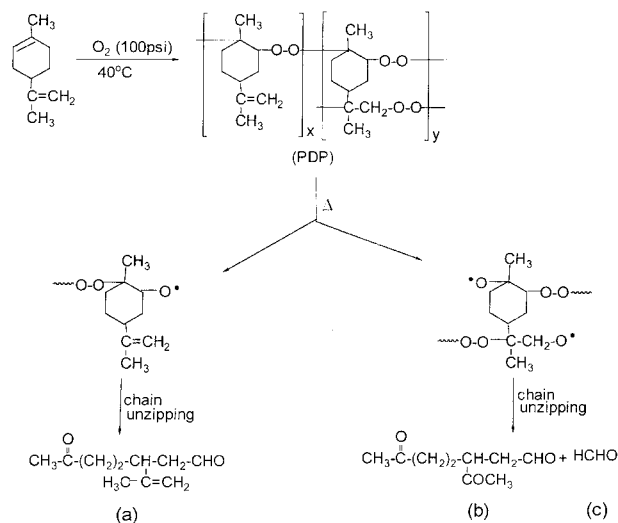
Kinetics of Dipentene Oxidation (in Absence of an Initiator)

Thermo oxidative polymerization of DP has been carried out at 40°C in the absence of an added initiator. There were no appreciable amounts of side products detected along with PDP. In the thermo-oxidative polymerization of DP, the rate of polymerization in terms of oxygen consumption, at various oxygen pressures, is shown in Figure 4. The oxygen consumption was found to be nonlinear with time exhibiting a knee point. It is noted from the Figure 4 that the rate of polymerization below the knee point (R_{p1}) is lower than the rate of polymerization above the knee point (R_{p2}), i.e., $R_{p2} > R_{p1}$. This observation is very similar to what we observed in the thermo-oxidative polymerization of α-methyl styrene (AMS).[18] Generally, in a free radical polymerization, at lower conversions, the R_p usually decreases with time but at very high conversion when viscosity of the system becomes sufficiently high, R_p increases with time due to Tormsdroff

Figure 2   TGA traces of PDP.

Table I Structural Assignments in the EI Mass Spectrum of PDP

Structure	m/z
$CH_2{=}\overset{\overset{\textstyle CH_3}{\textstyle\vert}}{C}{}^+$	41
$CH_3{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{}^+$	43
$CH_3{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{-}CH_2^+$	57
$CH_3{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{-}(CH_2)_2^+$	71
$CH_3{-}\overset{\overset{\textstyle CH_2}{\textstyle\Vert}}{C}{-}CH{=}CH{-}CH_2^+$	81
$CH_3{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{-}CH{=}CH{-}CH_2^+$	83
$CHO{-}CH_2{-}\overset{\overset{\textstyle CH_2}{\textstyle\Vert}}{C}{-}C{=}CH_2^+$	95
$CH_3{-}\overset{\overset{\textstyle CH_2{-}CHO}{\textstyle\vert}}{\underset{\underset{\textstyle CH_2}{\textstyle\Vert}}{C}}{-}CH{-}CH_2^+$	97
$CHO{-}CH_2{-}\overset{\overset{\textstyle COCH_3}{\textstyle\vert}}{CH}{}^+$	99
$CH_3{-}\overset{\overset{\textstyle CH_2}{\textstyle\Vert}}{C}{-}\overset{\overset{\textstyle CH_2}{\textstyle\Vert}}{C}{-}CH_2{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{}^+$	109
$CH_3{-}\overset{\overset{\textstyle CH_2{-}CHO}{\textstyle\vert}}{\underset{\underset{\textstyle CH_2}{\textstyle\Vert}}{C}}{-}CH{-}CH_2^+$	111
$CH_3{-}\overset{\overset{\textstyle CH_2{-}CHO}{\textstyle\vert}}{\underset{\underset{\textstyle CH_2}{\textstyle\Vert}}{C}}{-}CH{-}(CH_2)_2^+$	125
$CH_3{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{-}(CH_2)_2{-}\overset{\overset{\textstyle CH_2{-}CHO}{\textstyle\vert}}{CH}{}^+$	127
$CH_3{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{-}(CH_2)_2{-}CH{-}CH_2{-}\overset{\overset{\textstyle O}{\textstyle\Vert}}{C}{}^+$ $\underset{\underset{\textstyle CH_3}{\textstyle\vert}}{\overset{\overset{\textstyle }{\textstyle\vert}}{C}}{=}CH_2$	167

Scheme 1   Primary degradation products of PDP.

effect.[19] Because in the present investigation the conversions were kept below 5%, the increase in R_p with time can be attributed due to different kinds of "autoacceleration" as it is observed for AMS thermal oxidative polymerization. In the thermo-oxidative polymerization of DP the degradation products of PDP were found to accelerate the degradation of PDP similar to what is observed in AMS polymerization[18] where acetophenone accelerates the degradation of the formed
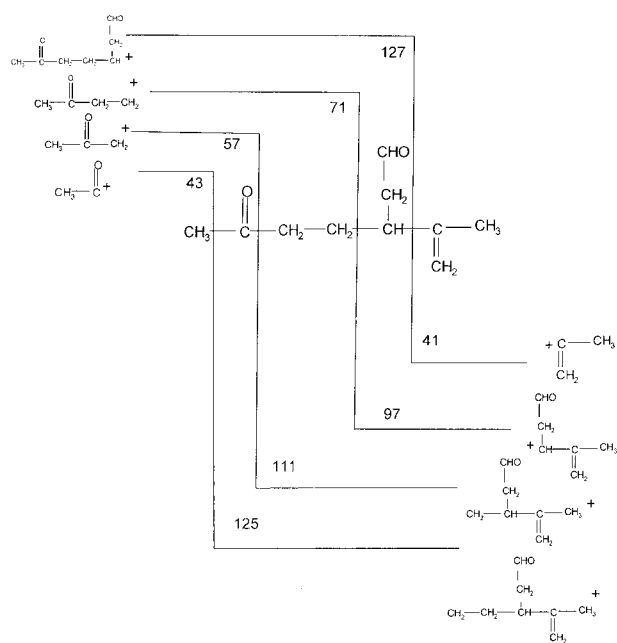
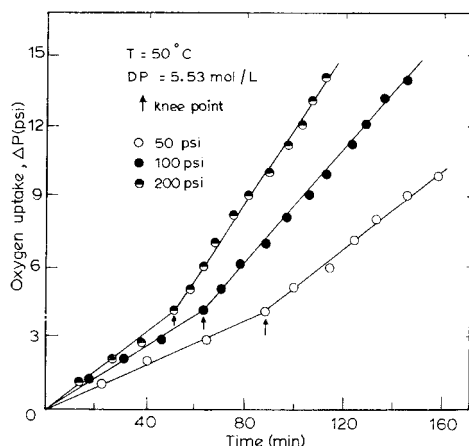**Scheme 2**   Secondary degradation products of structure (a).

Figure 4 Oxygen consumption (ΔP) as a function of time for the thermal oxidative polymerization of DP at 50, 100, and 200 psi.

PMSP. Hence, a similar mechanism is operating in thermal oxidative polymerization of DP also, where products of degradation bring about accelerated degradation of the formed polyperoxide generating more alkoxy radicals that eventually initiates the thermo-oxidative polymerization and bring about increase in R_p with time.

Table II summarizes the results of polymerization of DP at 50°C. The DP concentration variation experiments were carried out using chlorobenzene as a diluent. The exponents for monomer and oxygen were calculated from the slope of the plot of ln R_p vs. ln[M] and ln R_p vs. ln [O_2], respectively. R_{p1} and R_{p2} were found to be proportional to $[M]^{1.5}[O_2]^{0.5}$ and $[M]^{1.7}[O_2]^{0.2}$, respectively. Below the knee point the exponent values

of the monomer and oxygen were the normal exponent values expected for thermo-oxidative polymerization; hence, the kinetics of polymerization follows a normal behavior below the knee point. Above the knee point, the exponent values differ significantly from the expected normal values indicating a change in the mechanism of the thermo-oxidative polymerization of DP. This is very similar to the behavior that is observed for the thermo-oxidative polymerization of AMS.[18]

The autoacceleration emanates from the *in situ* slow degradation of the O—O bond of formed polyperoxides forming alkoxy radicals (RO$^\bullet$), which may further initiate along with the usual thermal initiation process. Again, the rate increases with temperature (Table III), and it shows autoacceleration polymerization at higher temperature. This anomaly can be explained only on the basis that more alkoxy radicals (i.e., initiating species) generated at higher temperatures. Hence, the knee point appears earlier with an increase in temperature, which proves autoacceleration mainly appears due to the formation of alkoxy radicals.

Oxidative Polymerization of DP in Presence of AIBN

Oxidative polymerization of DP has also been carried out in the presence of AIBN. The R_p at various AIBN concentrations are summarized in Table IV. Unexpectedly, the R_p is not proportional to $[AIBN]^{0.5}$. For determining AIBN exponent value, the ln–ln plot was found to be nonlinear; hence, it could not be determined accurately, but its ap-

Table II Effect of Oxygen Pressure and DP Concentration on the Thermal Oxidative Polymerization of DP[a]

[DP] (mol/L)	O_2 (psi)	R_{p1} (psi/min)	R_{p2} (psi/min)	R_{p1} [(mol/L)/h]	R_{p2} [(mol/L)/h]
2.51	100	0.025	0.043	0.042	0.072
3.77	100	0.045	0.093	0.076	0.158
4.27	100	0.060	0.121	0.102	0.205
5.03	100	0.066	0.156	0.112	0.264
5.53	100	0.068	0.171	0.116	0.289
6.28	100	0.069	0.188	0.117	0.318
5.53	50	0.045	0.169	0.076	0.286
5.53	150	0.071	0.198	0.121	0.336
5.53	200	0.084	0.206	0.142	0.349
5.53	250	0.103	0.231	0.175	0.391

[a] Temperature = 50°C; reaction time = 3 h; diluent = chlorobenzene.

Table III   Effect of Temperature on the Thermal Oxidative Polymerization of DP[a]

O_2 (psi)	T (°C)	R_{p1} (psi/min)	R_{p2} (psi/min)	R_{p1} [(mol/L)/h]	R_{p2} [(mol/L)/h]
100	45	0.040	0.100	0.069	0.172
100	50	0.069	0.188	0.117	0.318
100	60	0.129	0.333	0.212	0.547
100	65	0.140	0.370	0.227	0.599
100	70	0.170	0.460	0.271	0.735

[a] Reaction time = 3 h; [DP] = 6.28 mol/L.

proximate value is 0.2, which is different from the normal value of 0.5. The variation in the exponent value is attributed to a complex mechanism in thermo-oxidative polymerization; simultaneous AIBN initiation complicates the mechanism. The ratio of the actual to the theoretical yield was found was 0.2, indicating considerable degradation of PDP during the oxidative polymerization of DP, because the degradation products of PDP are volatile, which escaped along with the unreacted oxygen. This explains that the autoacceleration phenomenon is mainly governed by the generation of alkoxy radicals. Notwithstanding the effect on the induction time, the occurrence of autoacceleration per se is not affected by the added initiator.

In AMS oxidative polymerization,[18] R_{p1} and R_{p2} were the same above 60°C, but in DP polymerization R_{p1} was always lower than R_{p2}, even at 70°C, which clarifies that the acyclic double bond is more stable and reacts gradually with an increase in temperature, generating alkoxy radicals for the formation of the knee point.

CONCLUSION

PDP, having peroxy groups of different thermal stability in both the main chain and side chain, has been synthesized by the oxidative polymerization of DP with and without adding free radical initiator. The (mail-chain)–(side-chain) vinyl polyperoxides, having labile groups of different thermal stability, appears to be more attractive than relatively hazardous acid polyperoxides for this purpose. Besides, by controlling the polymerization temperature, it is possible to control the side chain peroxy groups, which may be subsequently used at higher temperatures for graft polymers.

Subsequently, the unique feature of DP thermal oxidative polymerization is its exhibition of "autoacceleration" during polymerization. Decomposition of polyperoxides (PDP) to alkoxy radicals appears to be the main cause of autoacceleration. This behavior can be used to our advantage for using them as low-temperature initiators and curatives.

Table IV   Effect of AIBN Concentration in the Oxidative Polymerization of DP[a]

Monomer (mol/L)	AIBN (mol/L)	R_{p1} (psi/min)	R_{p2} (psi/min)	R_{p1} [(mol/L)/h]	R_{p2} [(mol/L)/h]
5.53	0.005	0.010	0.180	0.107	0.253
5.53	0.010	0.071	0.230	0.121	0.390
5.53	0.017	0.086	0.240	0.145	0.407
5.53	0.024	0.126	0.250	0.214	0.424
5.53	0.030	0.130	0.260	0.220	0.441

[a] [O_2] = 100 psi; Temperature = 50°C; reaction time = 3 h.

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