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Regiospecific Radical Polymerization of a Tetrasubstituted Ethylene Monomer with Molecular Oxygen for the Synthesis of a New Degradable Polymer

Akikazu Matsumoto* and Shuji Taketani

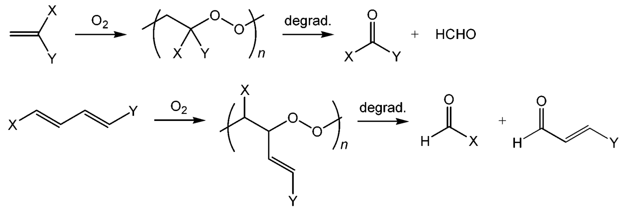
Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Received November 25, 2005; E-mail: matsumoto@a-chem.eng.osaka-cu.ac.jp

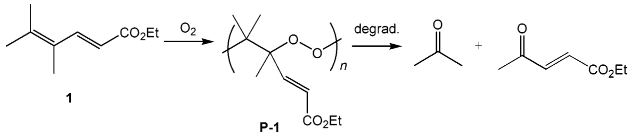
Molecular oxygen slowly reacts with organic compounds under atmospheric conditions because of its triplet electronic structure in the ground state.[1] Peroxide polymers with a labile O−O bond in their main chain are obtained from vinyl and diene monomers using molecular oxygen (Scheme 1).[2,3] They readily decompose via a radical chain reaction mechanism by various stimuli, such as heating, irradiation, and a redox system. Simultaneously, however, they yield formaldehyde as the degradation product as well as any other aldehydes or ketones according to their repeating structure. Such toxic and volatile products have prevented their use in practical applications, although peroxide polymers have the merits of facile polymer fabrication and well-controlled degradation via a radical chain process. To alter the degradation products from toxic and volatile aldehydes to acceptable ones, further substitution is required on the carbons adjacent to the peroxy unit in the main chain of the polymers. This means that the reacting vinyl moiety of the corresponding monomer should possess four substituents other than hydrogen. When the monomer **1** was used as the starting monomer with the simplest structure for the design of an environmentally friendly peroxide polymer, we found an unexpected and highly regiospecific propagation during the polymerization (Scheme 2). In general, the control of radical reactions of unsaturated compounds, including the propagation of diene monomers, has been observed under limited conditions[4]. We now report the synthesis of **P-1** via a highly regiospecific radical reaction and its degradation property.

The radical polymerization of **1** was carried out in 1,2-dichloroethane using a radical initiator with bubbling oxygen for 6 h at atmospheric pressure and 30 °C. The presence of multiple methyl groups on the double bond was predicted to significantly reduce its polymerization reactivity. In general, a tetrasubstituted ethylene monomer has an extremely low reactivity for not only homopolymerization but also copolymerizations. Nevertheless, the polymerization successfully proceeded in the presence of oxygen, resulting in the formation of an alternating copolymer with a relatively high molecular weight ($M_n = 5.6 \times 10^3$) in 13% yield. NMR spectroscopy revealed a regiospecific 5,4-repeating structure for **P-1**, as shown in Scheme 2. It has been reported that 2,3-dimethyl-2-butene (1,1,2,2-tetramethyl-substituted ethylene) undergoes autoxidation and effectively provides an unsaturated peroxy compound, 1,1,2-trimethyl-2-propenyl hydrogen peroxide, via hydrogen abstraction from a methyl group by a peroxy radical.[1c,5] An acryloyl substituent on the reacting double bond has the role of increasing the reactivity of **1** toward a peroxy radical. The highly controlled radical reactions of **1** and oxygen are discussed on the basis of the theoretical calculation results using a DFT method at the B3LYP level with a basis set of 6-311G*. The calculations were also carried out for the related diene monomers (Table 1), which show a similar excellent regiospecificity during the copolymerization with oxygen.

Scheme 1



Scheme 2



First, the Mulliken atomic charges were calculated for the diene moiety. The electron density on the C2 was much higher than that on the C5 for all the monomers. This suggests that the highly regioselective addition of a peroxy radical to the C5 carbon is not due to a difference in the electron density. Therefore, we calculated the heat of formation during the reactions of a methyl peroxy radical to diene monomers via two possible pathways, A and B, as shown in Scheme 3. These results are summarized in Table 1. All the reactions are exothermic (ΔH are negative) and the absolute values for path A were greater than those for path B. The values of $\Delta H_B - \Delta H_A$ were 8−11 kcal/mol, indicating the preference of the more stabilized structure of the allyl radicals formed via path A. This is due to conjugation to a carbonyl group as the substituent X.[4] During the copolymerization of **1**−**3** with oxygen, the 5,4-propagation is preferred over the 2,3-propagation despite the multiple substitution on the reacting double bond.

Next, we discuss the reaction of a delocalized allyl radical with molecular oxygen, that is, the selectivity of the 5,4- and 5,2-propagations. We calculated the spin density[6] for an allyl radical formed by the addition of a methyl peroxy radical. However, we found no preference of the 5,4-propagation. For example, the spin densities at the C4 and C2 carbons of **3** were the same for each other (1:1.04). Thus, the selectivity during the 5,4- and 5,2-propagations cannot be accounted for by the spin density of the allyl radical. It has been reported that the reactions of the carbon-centered radical with oxygen are reversible.[7−10] Recently, Pratt and Porter[11] determined the bond dissociation energies (BDE) of the carbon-to-oxygen bond for the substituted methyl peroxy radicals ($XCH_2OO\bullet$). They revealed that the BDE magnitude is independent of the stability of the carbon-centered radical ($XCH_2\bullet$) formed by β-dissociation releasing molecular oxygen, and that the C−OO• bond of peroxy radicals is stabilized by an electron-donating or conjugating group as X. The stabilization is induced by hyperconjugation between the substituents X and the σ_{C-O^*} orbital of the $XCH_2OO\bullet$ radical. When X is an electron-withdrawing group, the

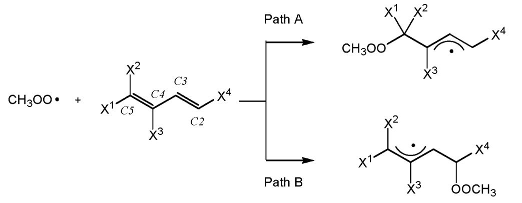
10.1021/ja0580385 CCC: $33.50

Table 1. Electron Density of Various Diene Monomers, Enthalpy Change for the Reaction with a Methyl Peroxy Radical, and BDE of the C−O Bond of the Formed Peroxy Radicals[a]

monomer	X^1	X^2	X^3	X^4	Mulliken atomic charge				ΔH_A (kcal/mol)	ΔH_B (kcal/mol)	$\Delta H_B - \Delta H_A$ (kcal/mol)	$BDE_{5,4}$	$BDE_{5,2}$
					C5	C4	C3	C2					
1	CH_3	CH_3	CH_3	CO_2CH_3	0.065	0.119	−0.198	−0.319	−11.92	−0.75	11.17	13.69	7.45
2	CH_3	CH_3	H	CO_2CH_3	0.113	−0.219	−0.142	−0.320	−9.58	−1.45	8.13	15.39	8.12
3	CH_3	H	H	CO_2CH_3	−0.155	−0.178	−0.130	−0.327	−9.95	−0.87	9.08	15.17	9.45
4	CH_3	H	H	CH_3								20.51	20.37

[a] (RO)B3LYP/6−311*//(U)B3LYP/6−311* level of theory. The addition of a methyl peroxy radical to diene monomers was used as the model reactions for the calculations. See also Scheme 3 and Figure 1.

Scheme 3



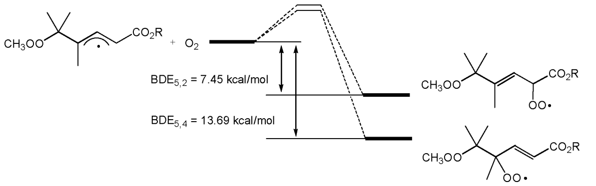


Figure 1. Energy diagram for the reaction of an allyl radical with molecular oxygen, resulting in the formation of the 5,2- and 5,4-adduct radicals, as the model reaction for the regiospecific propagation of **1**.

inductive effect of the substituent destabilizes the C−O bond of the peroxy radicals. We calculated the enthalpy change, that is, the BDE value, for the 5,2- and 5,4-propagation of the allyl radicals and oxygen at the (RO)BLYP/6-311G*//(U)BLYP/6-311G* level (Figure 1). The $BDE_{5,4}$ and $BDE_{5,2}$ values were 13.7−15.4 and 7.5−9.5 kcal/mol, respectively, for the reactions with **1**−**3** (Table 1). This indicates that the reverse reaction dissociation of the 5,2-adduct radical is faster than that of the 5,4-adduct radical by approximately 10^3. In contrast, the nonselective reaction of 2,4-hexadiene (**4**) has been confirmed by the calculation (Table 1) and previous experimental results.[3b]

Finally, we examined the degradation properties of **P-1** upon heating. The onset temperature of the degradation was revealed to be the lowest among the results for any of the other examined peroxide polymers;[3] the T_{95} and T_{init} values were 86.6 and 68.7 °C, respectively, by the TG/DTA measurements. The degradation is accelerated by the presence of methyl groups on the carbons adjacent to the peroxy linkage. To directly confirm the structure of the degradation products, a reaction was monitored by NMR spectroscopy during the isothermal degradation (see NMR spectra and Table S-3 in Supporting Information). The degradation products were exclusively acetone and ethyl 2-acetylacrylate (Scheme 2). The low polymer yield (13%) for the synthesis of **P-1** is partly due to the fast degradation during the polymerization.

In conclusion, we have fabricated a polymeric peroxide as a new kind of environmentally friendly and degradable polymer using a 1,3-diene derivative and oxygen as the starting materials in order to avoid the evolution of volatile and toxic compounds as degradation products. The exclusive 5,4-propagation is important for determining the thermal degradation property of the alternating copolymers because the existence of a 5,2-structure is not favored for efficient degradation. The theoretical calculations concluded that highly selective propagation reactions, such as the regiospecific reactions of a peroxy radical to diene monomers and an allyl radical to oxygen, are attributed to the enthalpies of the formation of the allyl radicals and the carbon−oxygen bond dissociation enthalpies of the peroxy radicals, respectively. The degradation of the peroxide polymers with a controlled repeating structure is triggered by various stimuli and leads to the formation of well-defined low-molecular-weight products. They include a significant potential for a wide range of uses in various fields of polymer chemistry and material science, including adhesion, coating, environmental, and medicinal chemistries.

Supporting Information Available: Warning, experimental procedures, DFT calculations, NMR spectra, degradation results, and TG/DTA thermograms (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0580385