PII: S0032-3861(97)00582-X

Polymer Vol. 39 No. 12, pp. 2677–2682, 1998

0032-3861/98/$19.00+0.00

Synthesis, characterisation and initiator properties of an amphiphilic diperoxide

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(Received 14 April 1997; revised 8 July 1997)

An amphiphilic diperoxide, palmitoyl (3-carboxy propionyl) sebacoyl diperoxide (PSD), was synthesised by the successive condensations of sebacoyl chloride with peroxypalmitic acid and monoperoxysuccinic acid in a pyridine medium and further characterised by i.r., ^{1}H n.m.r., MS as well as elemental analysis. The amphiphilic character of the diperoxide as surfactant was confirmed by the fact that the average area occupied by per PSD molecule at the air–water interface was found to be 0.31 nm^2 by the LB film method. The activation energy of the diperoxide for decomposition was determined by d.s.c. and calculated to be 142.7 kJ/mol. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: amphiphilic diperoxide; palmitoyl (3-carboxy propionyl) sebacoyl diperoxide (PSD); diacyl peroxide)

INTRODUCTION

It is well known that an initiator plays an important role in radical polymerisation since it determines the polymerisation rate, the molecular weight, and other characteristics of polymers. Because radical polymerisations can typically be carried out under relatively undemanding conditions, from an industrial stand-point, as compared with ionic or coordination polymerisations, many bi- and polyfunctional initiators have been studied intensively in recent years and used to preferentially prepare block copolymers[1,2]. As we know, water-soluble and oil-soluble monomers are specially difficult to directly copolymerise into amphiphilic block copolymers because of their significantly different polarity. To solve this problem, in previous papers we reported free radical interfacial copolymerisation as a facile and effective way for preparation of amphiphilic block copolymers[3,4]. In the new method, an amphiphilic bifunctional initiator, which has a hydrophobic part with a functional group generating free radicals and a hydrophilic part with an another functional group generating free radicals, is employed. Very recently, amphiphilic initiators (surface-active initiators) have attracted much interest because of being used as both initiator and emulsifier in emulsion polymerisation[5–7]. For example, Bohnenpoll *et al.*[7] not only synthesised a series of surface-active peroxy initiators but also used these initiators to initiate the emulsion polymerisation of some monomers. Although some amphiphilic initiators were prepared for emulsion polymerisation, all these initiators are monofunctional and were usually used in emulsion polymerisation. On the contrary, the amphiphilic initiators used in free radical interfacial copolymerisation are necessarily bifunctional. In the present paper, the synthesis, characterisation and properties of an amphiphilic diperoxide, palmitoyl (3-carboxy propionyl) sebacoyl diperoxide (PSD) are reported.

EXPERIMENTAL

Materials

Sebacoyl chloride was prepared from the corresponding diacid as described previously[8]. Monoperoxysuccinic acid was prepared according to the procedure described by Lombard *et al.*[9]. Eighty-five percent hydrogen peroxide was used as purchased from Tianjing Eastern Chemicals Plant, China. Pyridine was dried over potassium hydroxide and distilled prior to use. Diethyl ether was dried over sodium wire and filtered before use. Palmitic acid (analytically pure) and 20% fuming sulphuric acid (analytically pure) were used without further purification.

Measurements

^{1}H n.m.r. spectra were recorded with a Bruker ARX 400 (400 MHz) spectrometer. Proton chemical shifts, reported in parts per million, were referenced to tetramethylsilane directly as an internal standard. Multiplicities of resonance peaks are indicated as singlet (s), broad singlet (br s), triplet (t), multiplet (m), and broad multiplet (br m). Infrared (i.r.) spectra (NaCl, plates) were obtained at room temperature by using a Perkin-Elmer 1600 Series FTIR spectrometer and were reported in wavenumbers (4000–400 cm^{-1}). Mass spectra were obtained from Beijing Institute of Microchemistry, China. D.s.c. were performed on the amphiphilic diperoxide PSD using a Perkin-Elmer DSC-7 differential scanning calorimeter. The PSD sample was measured under four different heating rates: 8, 12, 16, 20°C/min. The pressure/area isotherm was recorded using a Langmuir-4 (Joyce-Loebl Inc.) at 20°C. The amphiphilic diperoxide

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PSD was dissolved in chloroform (4.71×10^{-4} mol/l). The subphase used was highly pure water, pH 5.6.

Synthesis of peroxypalmitic acid

Peroxypalmitic acid was prepared by the modified method of Berkowitz[10]. The preferred procedure is given in detail. (Caution: this reaction should be run behind a safety shield, and with the extreme precautions necessary when working with concentrated hydrogen peroxide.) To a 500-ml, round-bottomed flask equipped with a condenser and mechanical stirrer, were added 15.0 g (58.5 mmol) of palmitic acid and 180 ml of dichloromethane. After the complete dissolution of palmitic acid in dichloromethane, 12.5 g (31.3 mmol) of 85% hydrogen peroxide and 22.4 g of 20% fuming sulphuric acid were added dropwise, successively. The reaction mixture was stirred vigorously under reflux for 2.5 h, then cooled to room temperature and 200 ml of distilled water were added. The lower layer organic phase was evaporated under reduced pressure at room temperature to give 15.4 g crude product (96% purity determined iodometrically[11]; yield, 95.6%). The crude product was recrystallised from petroleum ether to yield analytically pure peroxypalmitic acid as long glistening needles, m.p. 59.4–60.5°C (lit.[12]: m.p. 60.3–60.8°C). I.r. (NaCl plate): 3265 (ν_{OH}, C(O)OOH), 2955, 2921, 2846 (ν_{C-H}, $C(CH_2)_{14}CH_3$), 1754, 1733 ($\nu_{C=O}$, C(O)OOH), 1467 (δ_{C-H}, $C(CH_2)_{14}CH_3$), 1401 (δ_{O-H}, C(O)OOH), 1264 (ν_{C-O}, C(O)OOH), 890, 878 (ν_{O-O}, C(O)OOH), 723 cm^{-1} ($\nu_{-(CH_2)_{14}-}$). ^1H n.m.r. (400 MHz, $CDCl_3$): δ, 11.37 (s, 1H, HOOC(O)), 2.44 (t, 2H, (O)CCH_2C), 1.70 (m, 2H, (O)CCH_2CH_2C), 1.25–1.33 (br m, 24H, $C(CH_2)_{12}CH_3$), 0.88 ppm (t, 3H, CH_3). Anal. calcd. for $C_{16}H_{32}O_3$ (272.43): C, 70.54; H, 11.84. Found: C, 70.47; H, 12.49.

Synthesis of PSD

Sebacoyl chloride (6.20 g, 25.9 mmol) was dissolved in dry diethyl ether (40 ml) and cooled to below 5°C. The solution of peroxypalmitic acid (3.40 g, 12.5 mmol) in dry diethyl ether (60 ml) and the solution of pyridine (1.30 g, 16.4 mmol) in dry diethyl ether (15 ml) were simultaneously added dropwise with vigorous stirring, while the temperature was maintained at 0–5°C. The mixture was stirred for an additional 3 h while it was allowed to warm to room temperature and filtered. When the filtrate was cooled at − 15°C, the intermediate product precipitated as a white solid from the ether solution. Subsequently the cooled filtrate was filtered at low temperature to give 3.30 g of white powder product.

Monoperoxysuccinic acid (1.85 g, 13.80 mmol) was dissolved in dry diethyl ether (65 ml). The solution of the above-prepared white powder (3.30 g, 6.95 mmol) in dry diethyl ether (150 ml) was then added at room temperature, followed by dropwise addition of pyridine solution (0.80 g, 10.1 mmol) in dry diethyl ether (20 ml), and the diacyl peroxide precipitated as it formed. After complete addition of pyridine, the slurry was stirred continuously for 2 h at room temperature and filtered. The precipitate was washed with distilled water and dried under vacuum at room temperature to give 2.9 g of white powder product (overall yield: 40.5%), m.p. 101–101.5°C (dec.). Peroxide oxygen content analysed iodometrically:[11] found, 5.66%; calculated, 5.59%. I.r. (NaCl plate): 3000–2500 (broad, ν_{OH}, COOH), 2918, 2849 (ν_{C-H}, CH_3 and CH_2), 1809, 1776 ($\nu_{C=O}$, –(O)C–O–O–C(O)–), 1697 ($\nu_{C=O}$, COOH), 1096, 1077 ($\nu_{(O)C-O-O-C(O)}$), 947 (δ_{O-H}, COOH), 896 cm^{-1} (ν_{O-O}). ^1H n.m.r. (400 MHz, $CDCl_3$): δ, 10 (br s, 1H, HOOC), 2.78(m, 4H, (O)CCH_2CH_2COOH), 2.42 (t, 6H, $CCH_2C(O)$), 1.71 (m, 6H, $CCH_2CC(O)$), 1.25–1.37 (br m, 32H, $C(CH_2)_{12}CH_3$ and (O)$CCC(CH_2)_4CCC(O)$), 0.87 ppm (t, 3H, CH_3). Anal. calcd. for $C_{30}H_{52}O_{10}$ (572.74): C, 62.91; H, 9.15. Found: C, 63.16; H, 9.13. FD-MS (*m/z*): 573 (M^+).

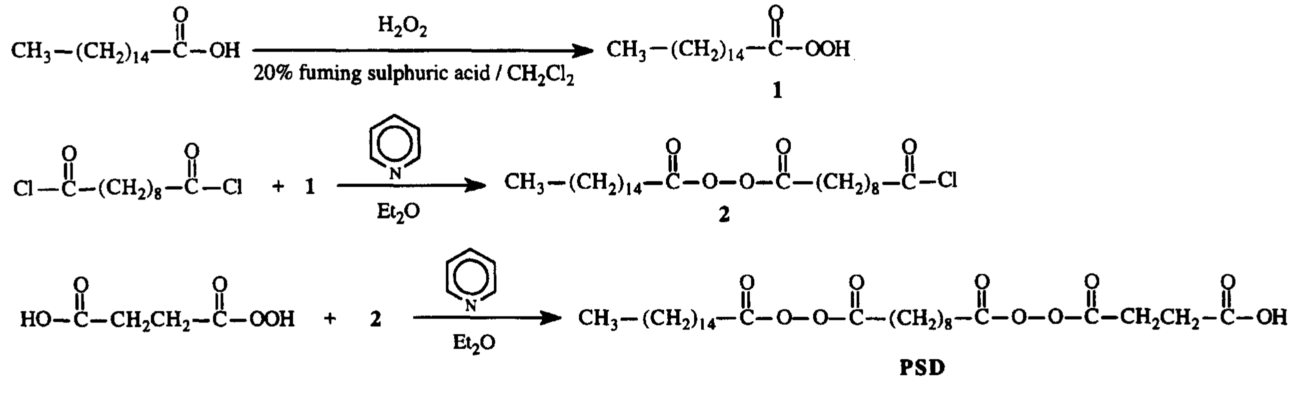
RESULTS AND DISCUSSION

The amphiphilic diperoxide, palmitoyl (3-carboxy propionyl) sebacoyl diperoxide (PSD) was synthesised according to *Scheme 1*.

Sebacoyl chloride[8] and monoperoxysuccinic acid[9] were prepared respectively according to the procedures described in the literature. The peroxypalmitic acid (**1**) was prepared by the oxidation of its corresponding carboxylic acid with a high concentration of hydrogen peroxide in the presence of fuming sulphuric acid catalyst using dichloromethane as reaction medium[10], and characterised by i.r., ^1H n.m.r. and elemental analysis.

The elemental analysis data of **1** is in good agreement with the theoretical calculation value. The i.r. spectrum of **1** shows the absorption bands at 1754 and 1733 cm^{-1} corresponding to the characteristic peaks of the peroxycarboxyl group in solid state. In the ^1H n.m.r. spectrum of **1**, as a further confirmation of the structure of **1**, the single sharp peak is attributable to the proton of the peroxycarboxyl group appearing at $\delta = 11.37$ ppm.

Subsequently, the intermediate **2** was prepared by the condensation reaction of peroxypalmitic acid **1** with an excess of sebacoyl chloride under the catalysis of pyridine, and characterised simply by i.r. due to its particular sensitivity to atmospheric moisture. The i.r. spectrum of **2**



$$CH_3-(CH_2)_{14}-C(=O)-OH \xrightarrow[\text{20\% fuming sulphuric acid / } CH_2Cl_2]{H_2O_2} CH_3-(CH_2)_{14}-C(=O)-OOH \;\; \mathbf{1}$$

$$Cl-C(=O)-(CH_2)_8-C(=O)-Cl + \mathbf{1} \xrightarrow[Et_2O]{\text{pyridine}} CH_3-(CH_2)_{14}-C(=O)-O-O-C(=O)-(CH_2)_8-C(=O)-Cl \;\; \mathbf{2}$$

$$HO-C(=O)-CH_2CH_2-C(=O)-OOH + \mathbf{2} \xrightarrow[Et_2O]{\text{pyridine}} CH_3-(CH_2)_{14}-C(=O)-O-O-C(=O)-(CH_2)_8-C(=O)-O-O-C(=O)-CH_2CH_2-C(=O)-OH \;\; \mathbf{PSD}$$

Scheme 1

(*Figure 1*) shows not only the characteristic peak of the remaining acyl chloride group at 1798 cm^{-1}, but also the characteristic peaks of the newly formed diacyl peroxy group at 1813 and 1783 cm^{-1}. In addition to these, the absorption band at 1700 cm^{-1} is attributable to the carboxyl group resulting from the easy hydrolysis of intermediate **2** in air. Therefore, intermediate **2** should be stored in a desiccator at low temperature for further use or used immediately.

In the last step, the condensation of the acyl chloride group of intermediate **2** with monoperoxysuccinic acid resulted in the formation of amphiphilic diperoxide PSD.

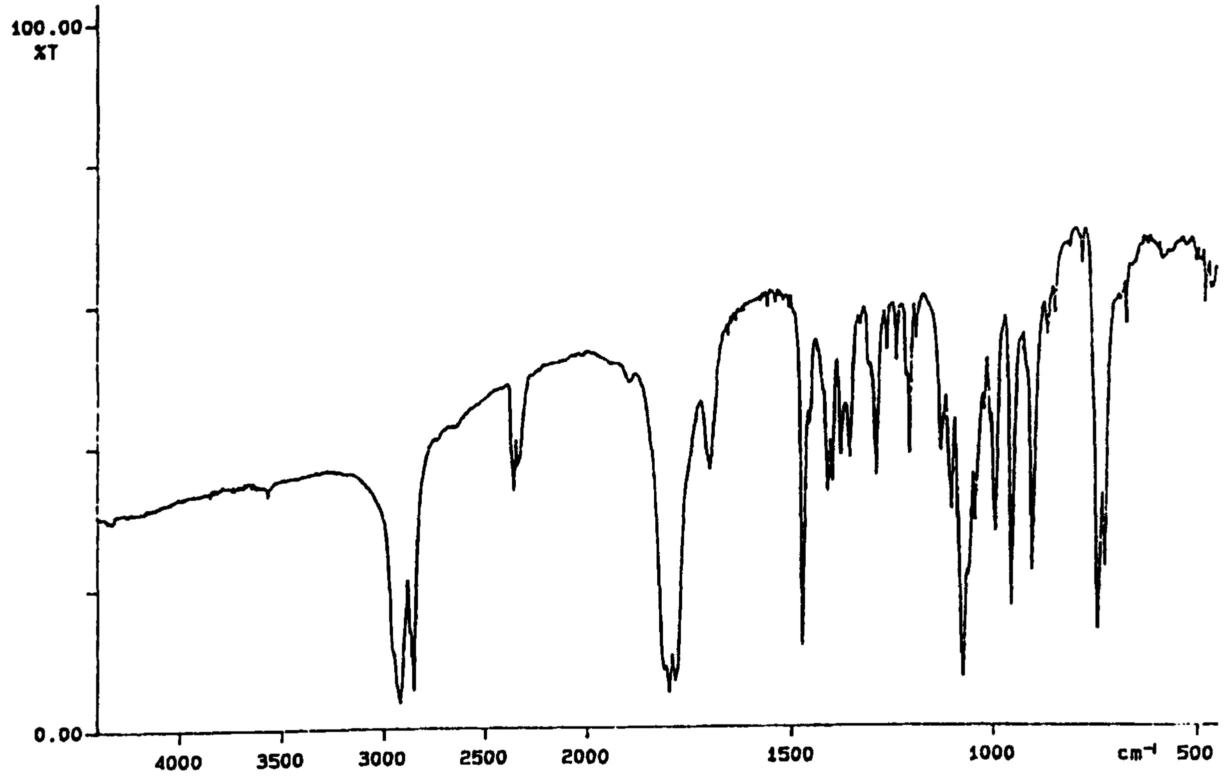


Figure 1 The i.r. spectrum of intermediate **2** (NACl plate)

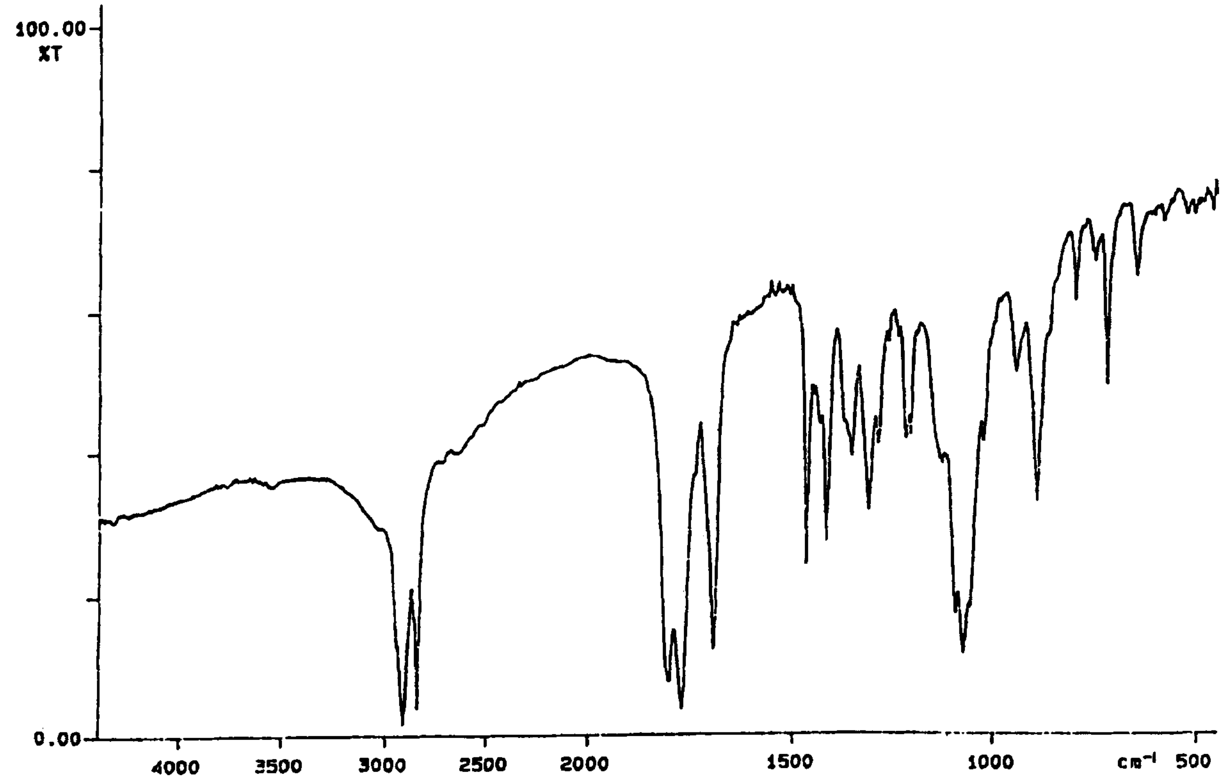


Figure 2 The i.r. spectrum of the synthesised amphiphilic diperoxide PSD (NACl plate)

Similarly to the synthesis of intermediate **2**, the reaction was carried out in anhydrous diethyl ether in the presence of pyridine catalyst at 0–5°C. The product was obtained by using distilled water to wash the hydrogen chloride pyridinium off the final precipitate mixture, and was dried under vacuum at room temperature. The synthesised diperoxide is quite safe in solid state, particularly in solution, and safely used in small quantities, and may be kept in the refrigerator for a long time.

The carbon and hydrogen contents of the product PSD, found experimentally (63.16% C, 9.13% H), are in good agreement with calculated values (62.91% C, 9.15% H). The i.r. spectrum of PSD (*Figure 2*) shows the doublet characteristic of the carbonyl group ($\upsilon_{C=O}$) in diacyl peroxides [–C(O)O–O–C(O)–] at 1809 and 1776 cm^{-1}, and the bands attributed to the –C(O)O–O–C(O)– at 1077 and 1098 cm^{-1}, to the peroxy links at 896 cm^{-1}. The other structurally functional groups are identified by absorption bands at 3000–2500 (υ_{OH}, COOH), 2918, 2849 (υ_{C-H}, CH$_3$ and CH$_2$), 1697 cm^{-1} ($\upsilon_{C=O}$, COOH).

The ^{1}H n.m.r. spectrum (*Figure 3*) shows the resonance signals corresponding to the proton types in the substance structure. $^{\delta}$ (ppm): 0.87 (t, 3H, CH_3), 1.25–1.37 (br m, 32H, $C(CH_2)_{12}CH_3$ and $(O)CCC(\underline{CH_2})_4CCC(O)$), 1.71 (m, 6H, $\underline{CCH_2CC(O)}$), 2.42 (t, 6H, $\underline{CCH_2C(O)}$), 2.78 (m, 4H, $\underline{(O)CCH_2CH_2COOH}$), 10.00 (br s, 1H, $\underline{H}OOC$).

Additionally, in the FD-MS spectrum of PSD, the molecular ion peak occurred at 573 *m*/*e*. The peroxide oxygen content of PSD determined iodometrically (5.59%) is also in agreement with the theoretical value (5.66%). All these results confirmed the structure of the amphiphilic diperoxide PSD.

Physicochemical properties of PSD

In order to show the physicochemical properties of PSD as a surfactant, we attempted to measure its critical micelle concentration (CMC) using the surface tension method. Because the structure of the diperoxide contains many more hydrophobic groups, it has poor solubility in aqueous solution. As a result, it is very difficult to monitor the change of the surface tension of the aqueous solution of PSD with concentration. So the amphiphilic nature of PSD was characterised alternatively by using an LB film method. If a solution of PSD in chloroform is spread at the air–water interface, a stable monolayer is formed. *Figure 4* shows the surface pressure (π)–area (A) isotherms of PSD on aqueous subphase at 20°C.

The π–A isotherm shows a gradual increase of the surface pressure π once the area A occupied by a single amphiphilic diperoxide molecule becomes smaller than 0.47 nm^2. Further compression is accompanied by an increasingly steeper rise in surface pressure until collapse. The corresponding A value is 0.31 nm^2 per amphiphilic molecule. This value is quite important for us, in order to ascertain indirectly the arrangement of the amphiphilic diperoxide molecules at the oil–water interface and to estimate some of the kinetic parameters of free radical interfacial copolymerisation. As can be seen, the synthesised diperoxide possesses amphiphilic character.

Thermal properties of PSD

For radical polymerisation, the activity of the initiator is of utmost importance because of its direct influences on the rate of polymerisation and the conversion of monomers, as well as on the structure of polymers. Therefore,

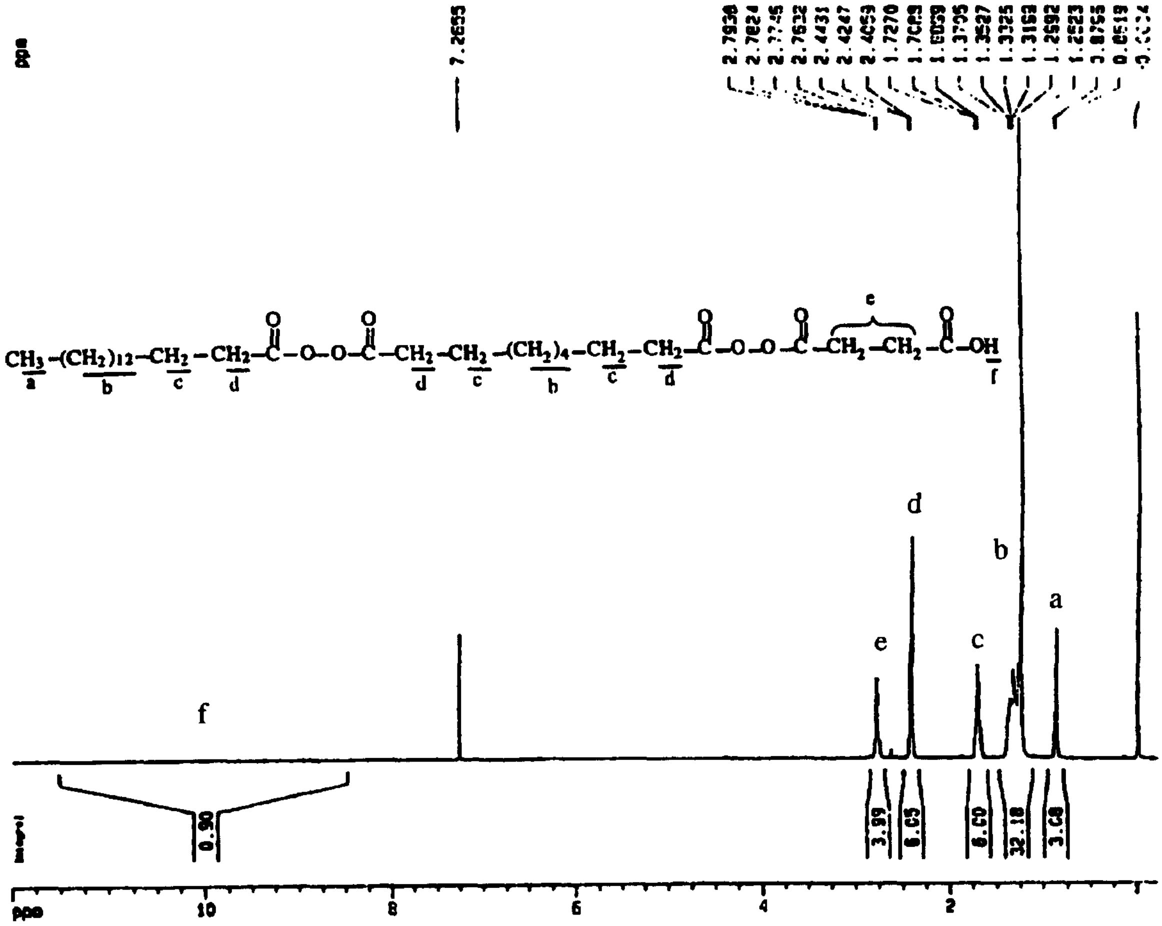


Figure 3 The ^{1}H n.m.r. spectrum of the synthesised amphiphilic diperoxide PSD ($CDCl_3$)

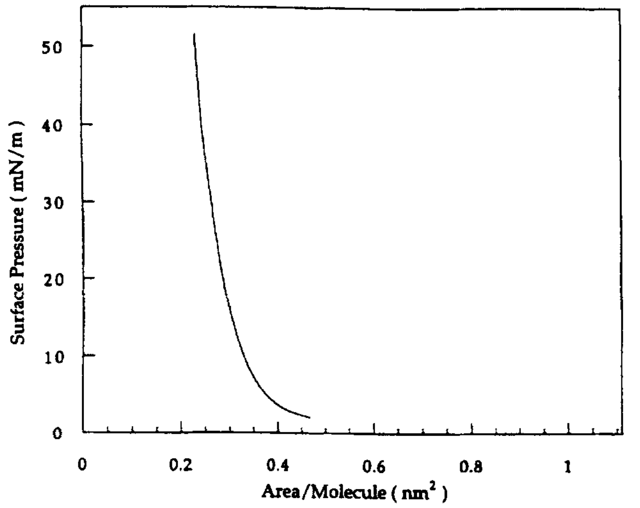


Figure 4 Surface pressure–area isotherms of PSD monolayer on a pure water subphase at 20°C

investigation of the activity of the amphiphilic diperoxide is beneficial to the studies of the mechanism and kinetic of free radical interfacial copolymerisation. One of the main aspects investigated is related to the initiator behaviour during decomposition. A decomposition kinetic study on the diperoxide PSD has been performed by means of d.s.c. This method can be used efficiently since there is no secondary reaction apart from the decomposition of the peroxy group. *Figure 5* shows the d.s.c. curves of the diperoxide PSD under various heating rates. However, the position of the exothermic peak due to the decomposition of peroxy units in the molecule shifted depending on the heating rate. *Table 1* summarises the temperatures at the maximum of the exotherm (T_p) of PSD under various heating rates.

Ozawa[13] and Haneda *et al.*[14] showed that the heating rate (ϕ) and absolute temperature (T) have the relationship given by equation (1):

$$\log\phi + 0.4567E_a/RT = \text{constant} \qquad (1)$$

where E_a is the activation energy and R the gas constant. The equation can be changed as follows

$$\log\phi = a\cdot(1/T) + b \qquad (2)$$

where $a = -0.4567E_a/R$.

The activation energy, thus, was calculated as the slope of plotting $\log\phi$ *versus* $1/T$. According to the slope of the relationship line between the reciprocal of the temperatures at the maximum of the exotherm (T_p) and logarithms of heating rate (ϕ) shown in *Figure 6*, the activation energy of the diperoxide for decomposition was calculated to be 142.7 kJ/mol which is close to the literature value (E_a = 127.2 kJ/mol) given for the commonly used diacyl peroxide lauroyl peroxide[15].

As reported previously, PSD was utilised as an amphiphilic bifunctional initiator in the free radical interfacial copolymerisation of acrylamide (AM) with *n*-butylmethacrylate (n-BMA) to prepare successfully the amphiphilic PAM/Pn-BMA block copolymer[3,4]. This proved that the diperoxide PSD certainly plays two roles, as both initiator and surfactant, in free radical interfacial copolymerisation. As can be seen, free radical interfacial copolymerisation has potential application prospects in the preparation of amphiphilic polymers.

CONCLUSIONS

An amphiphilic diperoxide palmitoyl (3-carboxy propionyl) sebacoyl diperoxide (PSD) was synthesised by the condensation reactions of sebacoyl chloride with peroxypalmitic acid and monoperoxysuccinic acid, successively. Its structure was confirmed by i.r., n.m.r., elemental analysis and FD-MS. Its amphiphilic character was characterised by the LB film method. It was found that the area occupied per

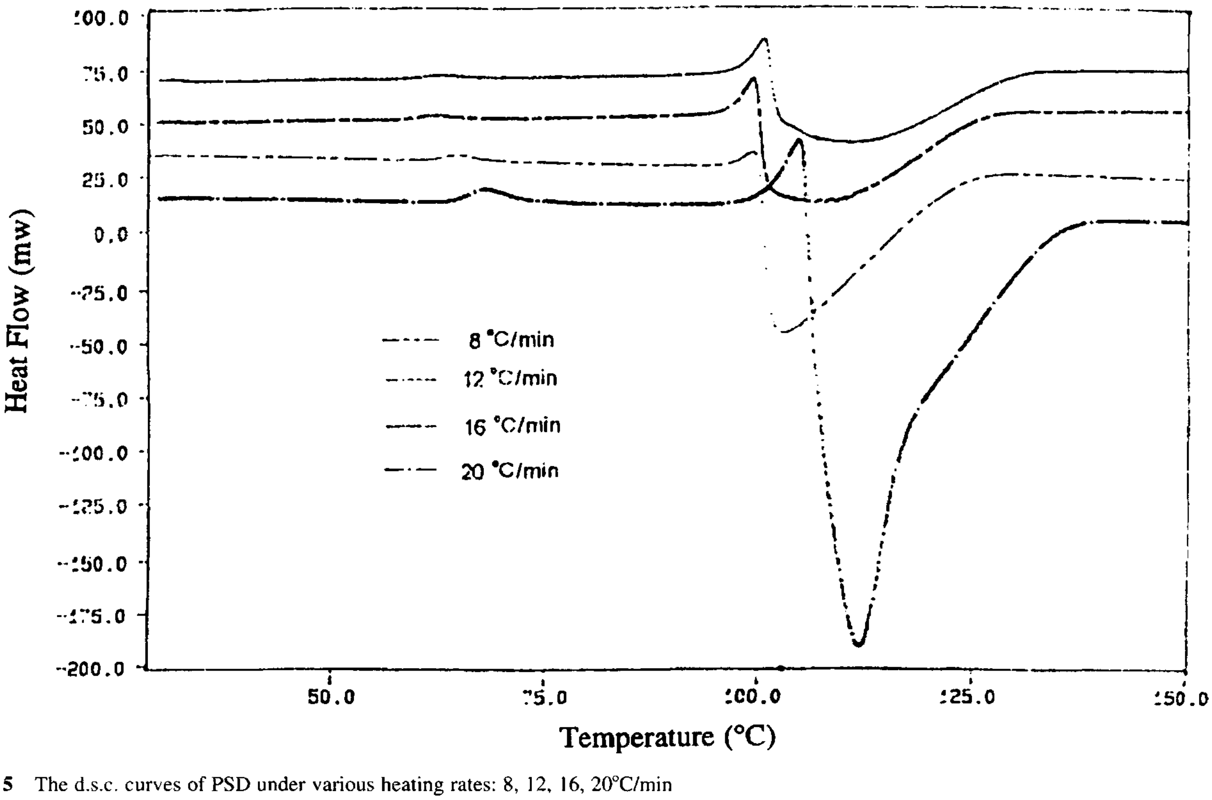


Figure 5 The d.s.c. curves of PSD under various heating rates: 8, 12, 16, 20°C/min

Table 1 The temperatures at the maximum of the exotherm (T_p) of PSD under various heating rates

Heating rate (°C/min)	T_p (°C)
8	102.908
12	105.925
16	108.080
20	110.300

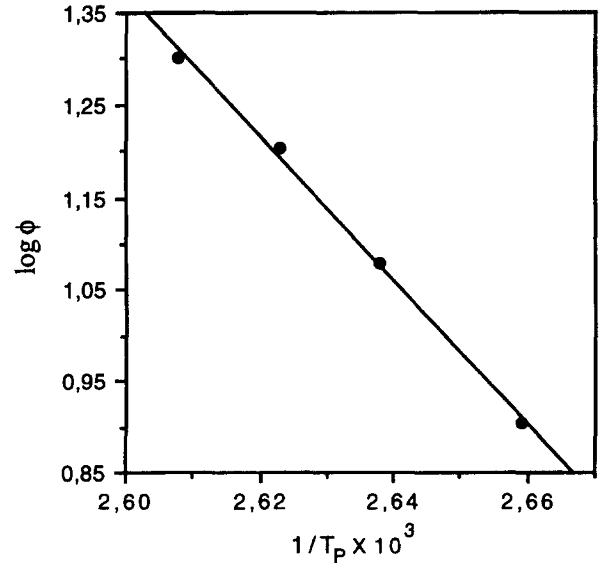


Figure 6 Typical relationship between reciprocal of the temperatures at the maximum of the exotherm (T_p) and logarithms of heating rate (ϕ)

diperoxide molecule at the air–water interface is 0.31 nm^2. The activation energy for decomposition was determined by differential scanning calorimetry and calculated to be 142.7 kJ/mol. As an amphiphilic bifunctional initiator, the diperoxide PSD is able to initiate the free radical interfacial copolymerisation of acrylamide with *n*-butylmethacrylate to give the amphiphilic PAM/Pn-BMA block copolymer. Detailed studies on the kinetics and mechanism of free radical interfacial copolymerisation are in progress.

ACKNOWLEDGEMENTS

We are grateful for the financial support from the National Natural Science Foundation of China.

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