Polymer 43 (2002) 2591–2594

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Structural characterization of maleic anhydride grafted polyethylene by ^{13}C NMR spectroscopy

Liqun Yang, Farao Zhang, Takashi Endo, Takahiro Hirotsu*

Institute for Marine Resources and Environmental Research, National Institute of Advanced Industrial Science and Technology, 2217-14 Hayashi-cho, Takamatsu 761-0395, Japan

Received 21 November 2001; received in revised form 14 December 2001; accepted 14 December 2001

Abstract

Maleic anhydride grafted polyethylene, [2,3-$^{13}C_2$] MA-*g*-PE, which was synthesized with ^{13}C labeled maleic anhydride [2,3-$^{13}C_2$] MA in solution, was characterized by ^{13}C NMR spectroscopy in order to make clear the structure of graft groups. The results reveal that [2,3-$^{13}C_2$] MA-*g*-PE has succinic anhydride oligomeric grafts with a terminal unsaturated MA ring in addition to well-known saturated succinic anhydride oligomeric grafts and that the former grafts are longer but fewer than the latter. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: ^{13}C NMR spectroscopy; Graft; [2,3-$^{13}C_2$] Maleic anhydride

1. Introduction

Polyethylene (PE) grafted with maleic anhydride (MA), MA-*g*-PE, exhibits enhanced compatibility in polymer alloys of PE with polar materials like cellulose and chitin [1], which are promising as new environmental protection plastics. However, the lack of well-confirmed experimental evidence has left obscure the molecular structure of MA groups grafted onto PE, mainly owing to the low graft degree [2]. From the theory of graft-polymerization of MA on PE proposed by Gaylord and Mehta [3], the macroradicals with different average graft chain lengths $m + 1$ and $n + 1$ probably undergo three main terminations: disproportionation, hydrogen abstraction and coupling (Scheme 1). MA being a strong electron acceptor causes a tendency towards disproportionation and hydrogen abstraction rather than coupling [4,5], suggesting that the possibility of structure III is very small.

In this study, we demonstrate the formation of succinic anhydride oligomeric grafts with a terminal unsaturated MA ring (oligo-MA, structure I in Scheme 1) in addition to well-known saturated succinic anhydride oligomeric grafts (oligo-SA, structure II in Scheme 1) [4] by solution state ^{13}C NMR spectroscopy.

2. Experimental

2.1. Reagents

[2,3-$^{13}C_2$] MA, isotopically enriched with 99% ^{13}C, and 1,1,2,2-tetracholoroethane-d_2 were purchased from ISOTEC Inc. Low molecular weight PE (lmPE) with M_w: ca. 4000 and M_n: ca. 1700 from GPC, was used, available commercially from Aldrich. *o*-Dichlorobenzene (*o*-DCB), dehydrated acetone (water content < 50 ppm), and hexamethyldisiloxane (HMDS) were bought from Wako.

2.2. Synthesis of [2,3-$^{13}C_2$] MA-g-lmPE

[2,3-$^{13}C_2$] MA (1 wt% of lmPE) was reacted with lmPE to yield the graft copolymer, [2,3-$^{13}C_2$] MA-*g*-lmPE, by using *tert*-butyl peroxide (10 wt% of lmPE) as an initiator in *o*-DCB under a nitrogen atmosphere at 170 °C for 1 h. The product was purified by dissolving in *o*-DCB and precipitating in boiling acetone two times, and then dried in vacuum at 100 °C overnight. Finally, the graft degree of [2,3-$^{13}C_2$] MA onto lmPE (defined as the ratio in number of the total labeled grafted carbons to the carbons on the lmPE backbone) was determined as ca. 0.05% from quantitative ^{13}C NMR analysis.

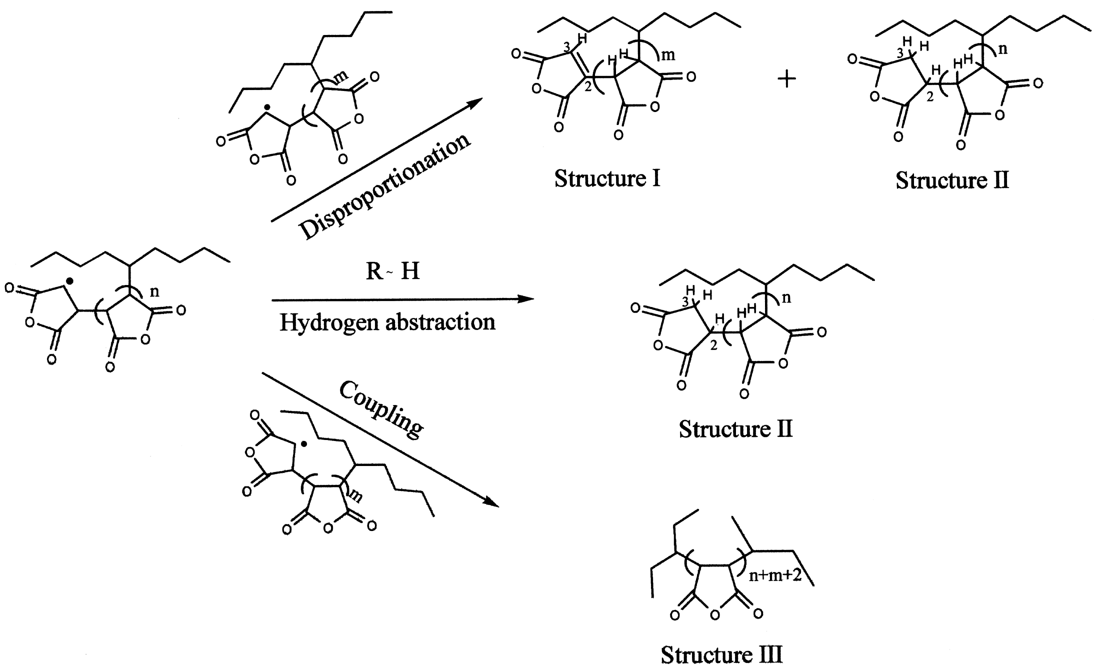
2.3. ^{13}C NMR measurement

Solution NMR spectra were recorded on a Varian Inova 400 spectrometer at 85 °C. A sample (175 mg) was

---

* Corresponding author. Tel.: +81-87-869-3562; fax: +81-87-869-3553.
E-mail address: takahiro-hirotsu@aist.go.jp (T. Hirotsu).

0032-3861/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00802-3



Scheme 1.

dissolved in 0.7 ml of 1,1,2,2-tetrachloroethane-d_2 in a 5 mm ϕ NMR tube. ^1H NMR spectra were obtained at 399.80 MHz and ^{13}C NMR spectra at 100.53 MHz. In order to control the nuclear overhauser effect (NOE), a relaxation–delay time of 10 s ($>5T_1$ of the labeled carbons) was used in acquiring quantitative inverse-gated ^1H decoupled ^{13}C NMR spectra. DEPT was used to distinguish the labeled carbon signals of methine and methylene in grafted groups. The ^{13}C chemical shifts were referred internally to the major backbone methylene carbon resonance that was taken as 30.00 ppm from TMS [6], and the ^1H chemical shifts referred to internal standard HMDS.

3. Results and discussion

Inverse-gated ^1H decoupled ^{13}C NMR spectra of [2,3-$^{13}C_2$] MA-*g*-lmPE are shown for the low and high fields in Figs. 1 and 2, respectively, and compared with those of lmPE. For the low field, we have observed for the first time two new pairs of signals on an inverse-gated ^1H decoupled ^{13}C NMR spectrum of [2,3-$^{13}C_2$] MA-*g*-lmPE as clearly shown in Fig. 1. Compared with ^{13}C NMR spectra of lmPE and ^{13}C unlabeled MA-*g*-lmPE (Fig. 1(a) and (c)), [2,3-$^{13}C_2$] MA-*g*-lmPE exhibit two pairs of signals around 158 and 128 ppm that appear around the chemical shift of

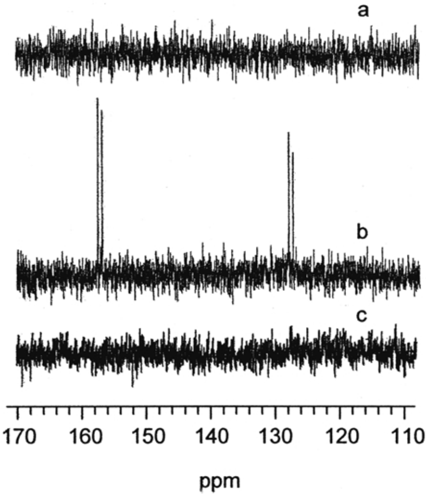


Fig. 1. Inverse-gated ^1H decoupled ^{13}C NMR spectra in the low field: lmPE (a), [2,3-$^{13}C_2$] MA-*g*-lmPE (added MA/lmPE: 1 wt%) (b), and ^{13}C unlabeled MA-*g*-lmPE (added MA/lmPE: 25 wt%) (c).

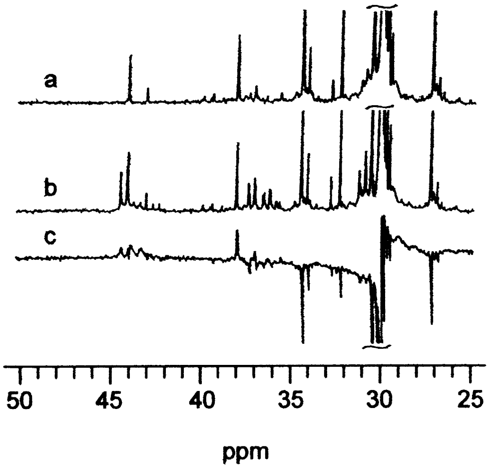


Fig. 2. Inverse-gated ^1H decoupled ^{13}C NMR spectra in the high field: lmPE (a) and [2,3-$^{13}C_2$] MA-*g*-lmPE (b); A DEPT spectrum of [2,3-$^{13}C_2$] MA-*g*-lmPE (c).

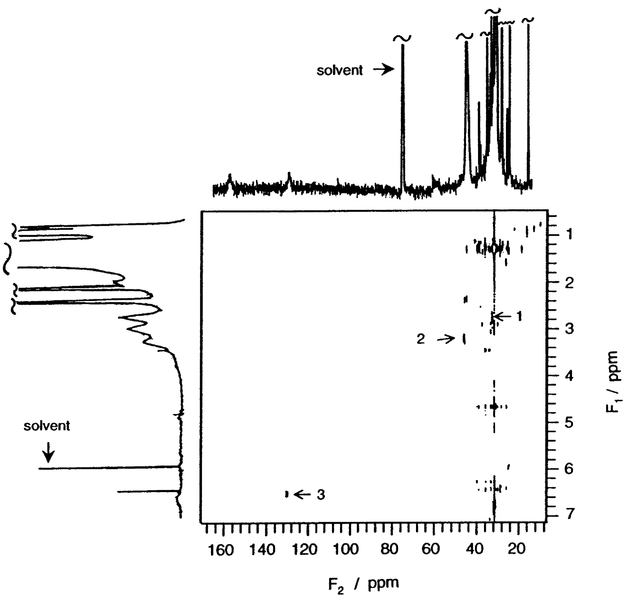


Fig. 3. An H,C-COSY spectrum of [2,3-$^{13}C_2$] MA-*g*-lmPE.

olefin (Fig. 1(b)) [7]. These signals are characteristic of an AX spin system $\{\Delta v/J = 46\ (>6)$ where Δv is the chemical shift difference between nuclei (2979.9 Hz) and J is coupling constant (65.20 Hz)$\}$ [7], which indicates that there are inequivalent labeled carbons attached to lmPE chain. The value of $^1J_{cc}$ coupling is typical for an sp^2–sp^2 $^{13}C{=}^{13}C$ double bond coupling [8]. The H, C-COSY 2D analysis directly shows that the peaks at 158 and 128 ppm are due to the ring quaternary and methine carbons, respectively, in Fig. 3, where the F_1 and F_2 axes are for ^{1}H and ^{13}C chemical shifts, respectively. It is found that plot 3 with $F_2 = 128$ ppm has a correlated peak at $F_1 = 6.43$ ppm, which can be assigned to the proton connected with a double bond carbon atom (C3 in Structure I) [7]. Conversely, the lack of a correlated ^{1}H peak with the ^{13}C signal at 158 ppm means the other double bond carbon is quaternary (C2 in Structure I). Therefore, the results show that [2,3-$^{13}C_2$] MA-*g*-lmPE has graft groups with an unsaturated labeled $^{13}C{=}^{13}C$ double bond terminal ring (Structure I in Scheme 1; oligo-MA).

For the high field in Fig. 2(b), resonances at 32–30 and 46–42 ppm have been assigned to the methylene carbon (C3) on the terminal ring of oligo-SA (Structure II in Scheme 1) and the methine carbons in the grafts of [2,3-$^{13}C_2$] MA-*g*-lmPE, respectively [4,9,10]. It is noted that the ^{13}C signal at 46–42 ppm is due to the methine carbons not only in oligo-SA but also in oligo-MA. This assignment is consistent with the H, C-COSY 2D spectrum of [2,3-$^{13}C_2$] MA-*g*-lmPE in Fig. 3. Plot 1 (F_2: 32–30 ppm) and plot 2 (F_2: 46–42 ppm) correlate well with methylene (F_1: 2.70 ppm) and methine protons (F_1: 3.24 ppm), respectively, which are in agreement with ^{1}H chemical shifts of the methylene (2.83 ppm) and methine protons (3.30–3.20 ppm) in the succinic anhydride ring of a model compound pristane-*g*-maleic anhydride [10]. Moreover, it can be confirmed from DEPT that the signal of the labeled ring methine is up while the signal of the labeled ring methylene is down when θ is 135° (Fig. 2(c)). Accordingly, the present results clearly demonstrate that [2,3-$^{13}C_2$] MA-*g*-lmPE contains oligo-MA with a terminal unsaturated ring (Structure I) as well as oligo-SA (Structure II), the only graft structure that had been observed prior to this work.

From the integrated responses in quantitative inverse-gated ^{1}H decoupled ^{13}C NMR spectra (Figs. 1(b) and 2(b)) after the correction for lmPE background (Figs. 1(a) and 2(a)), we may estimate the graft chain lengths of oligo-MA ($m + 1$ in Structure I) and oligo-SA ($n + 1$ in Structure 2), and the molar ratio of oligo-MA to oligo-SA (R_M/R_S). For this examination, we make two assumptions: (1) the types of graft groups are oligo-MA and oligo-SA, and (2) the numbers of quaternary-, methine- and methylene-carbons in oligo-MA and oligo-SA are proportional to the integration strengths of the corresponding ^{13}C NMR peaks. Taking account of the structure of oligo-MA and oligo-SA, we can derive the following equations:

$$N_{CH} = N_{CH(M)} + N_{CH(S)} \tag{1}$$

$$N_{CH(M)}/N_{C3(M)} = N_{CH(M)}/N_{C2(M)} = 2m/1 \tag{2}$$

$$N_{CH(S)}/N_{C3(S)} = (2n + 1)/1 \tag{3}$$

where N is the number of carbons; the subscripts CH(M) and CH(S) denote methine carbons in oligo-MA and oligo-SA, respectively, and accordingly the subscript CH is methine carbons in both of the grafts; the subscripts C2(M) and C3(M) denote the C2 and C3 carbons in oligo-MA, and C3(S) the C3 carbon in oligo-SA. From Eqs. (1)–(3), Eq. (4) is derived:

$$n + (N_{C3(M)}/N_{C3(S)})m = 1/2(N_{CH}/N_{C3(S)} - 1) \tag{4}$$

Based on assumption (2), Eq. (4) is equivalent to the following relation:

$$n + (I_{C3(M)}/I_{C3(S)})m = 1/2(I_{CH}/I_{C3(S)} - 1) \tag{5}$$

where I is the integrated carbon response. This equation shows the relation between the chain lengths of oligo-MA and oligo-SA. However, because the signal due to the methine carbons in oligo-MA is not distinguished from that in oligo-SA (Fig. 2(b)), we cannot estimate the values of m and n exactly. On the other hand, the molar ratio of oligo-MA to oligo-SA is given by Eq. (6):

$$R_M/R_S = N_{C3(M)}/N_{C3(S)} = I_{C3(M)}/I_{C3(S)} \tag{6}$$

The experimental values of $I_{C3(M)}/I_{C3(S)} = 0.05$ and $I_{CH}/I_{C3(S)} = 2.36$ yield $R_M/R_S = 1/20$ and the following equation:

$$n + 0.05m = 0.68 \tag{7}$$

Thus, m varies from 13.60 to 0 with the change of n from 0 to 0.68. Although we cannot determine exactly the values of *m* and *n* at present, we may estimate that *m* is greater than *n*, i.e. the average graft chain of oligo-MA is longer than that of oligo-SA. Furthermore, $R_M/R_S = 1/20$indicates that the number of shorter oligo-SA graft groups is 20 times greater than that of longer oligo-MA graft groups. This may be due to the strong termination of the shorter grafting macroradicals by hydrogen abstraction (Scheme 1) because of MA being a strong electron acceptor. Further experiments are in progress and the results will be described in detail elsewhere.

4. Conclusions

[2,3-$^{13}C_2$] MA-*g*-lmPE synthesized in solution has longer but fewer oligo-MA graft groups with a terminal unsaturated maleic anhydride ring, as well as shorter but more oligo-SA ones consisting of saturated succinic anhydride rings.

References

[1] Zhang F, Qiu W, Yang L, Endo T, Hirotsu T. J Mater Chem 2002;12:24.

[2] Malaika SA. Reactive modifiers for polymers. London: Blackie Academic and Professional, 1997.

[3] Gaylord NG, Mehta M. J Polym Sci Polym Lett Ed 1982;20:481.

[4] Heinen W, Rosenmoller CH, Wenzel CB, De Groot HJM, Lugtenburg J. Macromolecules 1996;29:1151.

[5] Gaylord NG, Mehta M, Mehta R. J Appl Polym Sci 1987;33:2549.

[6] Griselda BG, Robert FS, Raquel SM, Fernanda FN. Macromolecules 1999;32:1620.

[7] Ling Y. Structural identification of organic compounds and organic spectroscopy. Beijing: Science Press, 2000.

[8] Abraham RJ, Fisher J, Loftus P. Introduction to NMR spectroscopy. New York: John Wiley & Sons Ltd, 1999.

[9] Heinen W, Erkens SW, Van Duin M, Lugtenburg J. J Polym Sci Part A: Polym Chem 1999;37:4368.

[10] Ranganathan S, Baker WE, Russell KE, Whitney RA. J Polym Sci Part A: Polym Chem 1999;37:3817.