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# Phase structure of ethylene–dimethylaminoethyl methacrylate copolymers and its relation to comonomer content as studied by solid-state high-resolution $^{13}C$ n.m.r. spectroscopy

**Hui-Jun Luo[a], Qun Chen[a,*], Guang Yang[a] and Duanfu Xu[b]**
[a] *Analytical Centre, East China Normal University, Shanghai 200062, China*
[b] *Institute of Chemistry, Academia Sinica, Beijing 100080, China*
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The phase structures of a series of ethylene–dimethylaminoethyl methacrylate (EDAM) copolymer samples were investigated by solid-state high-resolution $^{13}C$ n.m.r. spectroscopy. It is found that at least the $\alpha$ and $\beta$ methylene units relative to the tertiary carbon of dimethylaminoethyl methacrylate (DAM) along the molecular chain as well as DAM comonomer units are located outside the crystalline region. The $^{13}C$ CP–MAS spectra also reveal that with increasing DAM content, the ratio of monoclinic to orthorhombic crystals increases as well as the ratio of interfacial to crystalline regions. © 1997 Elsevier Science Ltd.

**(Keywords: EDAM copolymer; phase structure; $^{13}C$ n.m.r.)**

## INTRODUCTION

As is well known, the phase structures of semicrystalline copolymers have a great influence on the ultimate properties of the materials and have been subjected to extensive studies in past decades[1–3]. Recently, a series of semicrystalline ethylene copolymers, ethylene–dimethylaminoethyl methacrylate (EDAM), have received widespread attention. Ohmae *et al.*[4] have reported systematic work on EDAM, in which they correlated the crystalline structures with the content of comonomer units. In our previous work[5], we found that for a series of EDAM samples crystallized under the same conditions, the degree of crystallinity varies linearly with the number-average ethylene sequence length of the samples. The above results indicate that the content and distribution of comonomer units play important roles in determining the phase structure. However, despite extensive investigations, there are still some unsolved problems concerning the phase structures of EDAM copolymers. For example, the morphological partitioning of dimethylaminoethyl methacrylate(DAM), which is important for understanding the crystallization processes and the resulting phase structure, is still unclear. The phase structures of EDAM, which are rather complex because of the existence of two types of crystalline phase, an interfacial region and an amorphous region, are still not well defined. There is a need to study the phase structure of EDAM in depth and correlate it with the chain structure.

The aim of this work was to study the phase structure of EDAM copolymers in more detail by solid-state high-resolution $^{13}C$ n.m.r. spectroscopy. The reasons for the choice of this technique are as follows: (1) it has been used effectively to discriminate different phase structures, including different crystallographic forms of polyethylene[6–8]; and (2) it has been applied successfully to determine the morphological partitioning of short branches, cross-links and chain ends in low-density and cross-linked polyethylenes[9–11]. Basically, it may also be applicable to studying the morphological partitioning of comonomer units in ethylene copolymers.

## EXPERIMENTAL

### *Materials*

EDAM copolymer samples were obtained from Sumitomo Chemical; the synthesis procedures are described elsewhere[4]. *Table 1* lists the molecular characteristics of the six EDAM samples studied in this work. The molecular weights were reported by Ohmae *et al.*[4] and the DAM contents and number-average ethylene sequence lengths ($L_e$, counted per $CH_2CH_2$ unit) were determined by $^{13}C$ high-resolution n.m.r. in our previous work[5]. Samples were dissolved in chloroform at a concentration of 15 wt%, precipitated from solution by adding acetone and then dried in vacuum to constant weight for $^{13}C$ n.m.r measurements.

### *N.m.r. measurements*

The $^{13}C$ CP–MAS (cross-polarization and magic-angle spinning) and $^{13}C$ DD–MAS (dipolar decoupling and magic-angle spinning) n.m.r. measurements were carried out on a Bruker AMX-4000 spectrometer operating at 100.61 MHz at room temperature. The magic-angle spinning rate was ~5 kHz in all measurements and the contact time was 2 ms in CP experiments. The $^{13}C$ chemical shifts were determined from the higher field signal (29.5 ppm) of adamantane relative to tetramethylsilane (TMS).

The non-crystalline spectra were obtained by the $^{13}C$

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[*] To whom correspondence should be addressed

**Table 1** Structural characterizations of EDAM copolymers

| Sample | DAM content (mol%) | $M_n$ ($10^4$) | $M_w$ ($10^4$) | $L_e$ |
|---|---|---|---|---|
| DA3014 | 3.6 | 7.80 | 25.4 | 27.2 |
| DA3023 | 3.9 | 2.43 | 8.88 | — |
| DA3031 | 4.1 | 2.94 | 8.29 | 24.3 |
| DA3011 | 4.4 | 2.64 | 11.2 | 22.3 |
| DA3002 | 6.7 | 1.50 | 3.20 | 14.1 |
| DA3032 | 10.7 | 3.37 | 7.63 | 8.8 |

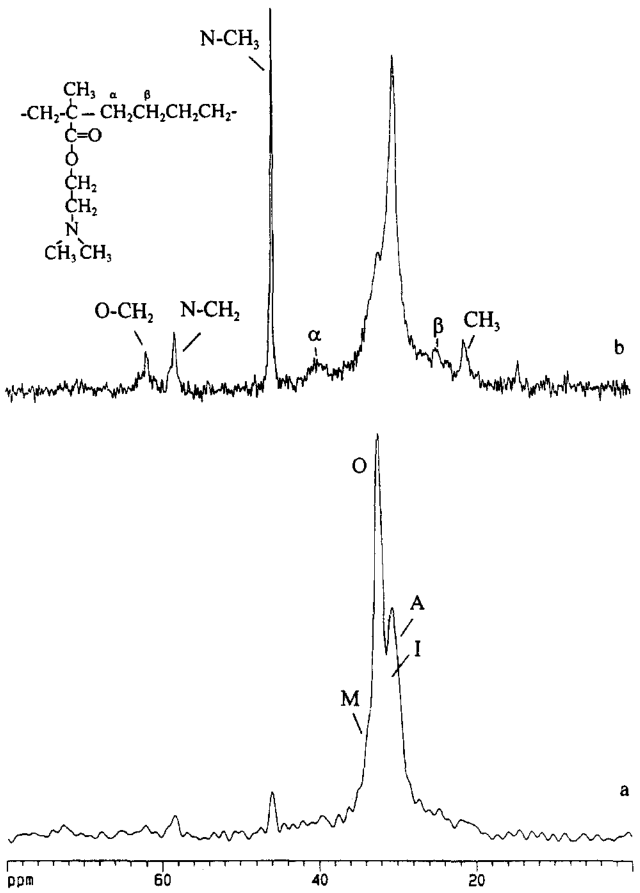
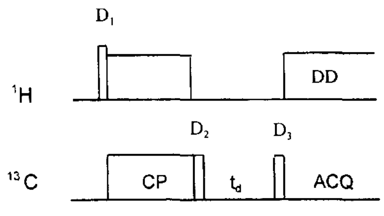


**Figure 1** $^{13}C$ CP-MAS (a) and DD-MAS (b) spectra of DA3002; M, O, I and A represent monoclinic and orthorhombic crystalline, interfacial and amorphous signals respectively



**Scheme 1**

DD-MAS method[12]. Carbon magnetization was excited by 90° pulse and then observed in the presence of high-power proton decoupling. The pulse interval was chosen as 3 s, which is longer than the $^{13}C$ spin-lattice time $T_1$ of the non-crystalline phase but much shorter than that of the crystalline phases. Thus the crystalline signals were saturated in signal accumulation and greatly suppressed in the spectrum obtained.

The 'pure crystalline' $^{13}C$ spectra acquired using a Torchia pulse sequence[11,13] were recorded with a Bruker DSX-300 spectrometer operating at 75.47 MHz. *Scheme 1* shows the Torchia pulse sequence, in which $D_1$ represents the $^1H$ 90° pulse and $D_2$ and $D_3$ represent the $^{13}C$ 90° pulses. The interval $t_d$ was set at 6 s to allow complete decay of the non-crystalline signals.

## RESULTS AND DISCUSSION

### *Morphological partitioning of EDAM*

*Figure 1a* and *b* show the $^{13}C$ CP-MAS and DD-MAS spectra of sample DA3002 from 0 to 90 ppm. Only the signal of carbonyl carbon is excluded. Peak assignments were made according to the previous solution-n.m.r. results on the same series of sample[4] and are also shown in *Figure 1*. As reported previously[8,14], the $^{13}C$ CP-MAS spectrum of polyethylene (PE) often consists of orthorhombic and monoclinic crystalline signals, an interfacial signal and an amorphous signal. All these signals are observed in *Figure 1a* and labelled O, M, I and A respectively.

The basic method of determining the phase partitioning of DAM comonomer units is to obtain 'pure crystalline' and 'pure non-crystalline' spectra of EDAM samples, as used for morphological partitioning of short branches, chain ends and cross-links in low-density or cross-linked polyethylenes. Various methods[9–11,15] have been suggested for acquiring the 'pure crystalline' and 'pure non-crystalline' spectra of polyethylene. All these methods have the common characteristic of utilizing the difference between the relaxation times of protons or carbons in different phases. For polyethylenes, it is known that the $^{13}C$ spin–lattice relaxation time $T_1$ of the crystalline phase is usually $> 1000$ s, whereas that of the non-crystalline phase is usually $< 1$ s at room temperature[8]. Such a large difference is also believed to be exhibited by EDAM copolymers and therefore can be used to annul either the crystalline or the non-crystalline signals.

*Figure 1b* is the non-crystalline spectrum of DA3002 obtained by the $^{13}C$ DD-MAS method. In comparison with that in *Figure 1a*, the relative intensity of the orthorhombic crystalline signal is greatly reduced. On the other hand, the relative intensities of the signals corresponding to the non-crystalline methylenes, DAM units and $\alpha$ and $\beta$ carbons are greatly enhanced. Similar results were also found for the other EDAM samples listed in *Table 1*, indicating that for EDAM copolymers not only the DAM comonomer units but also two $CH_2$ units neighbouring the DAM along the ethylene sequences are mostly located outside the crystalline regions.

To confirm this result, pure crystalline spectra were measured by employing a Torchia pulse sequence (*Scheme 1*). The Torchia pulse works in such a way that with increasing time interval $t_d$, the signals with short $^{13}C$ $T_1$ decay first. Therefore if $t_d$ is chosen to be much longer than the $^{13}C$ $T_1$ of the non-crystalline region but much shorter than that of the crystalline region, the non-crystalline signals can be annulled without distinct influence on the signal-to-noise ratio of the crystalline signals. *Figure 2* shows the $^{13}C$ crystalline spectrum of DA3002 obtained by this method. It can easily be seen that the signals corresponding to the non-crystalline methylenes, DAM units and the $\alpha$, $\beta$ carbons disappeared from the spectrum, indicating further that the DAM units and the $\alpha$ and $\beta$ methylene carbons are excluded from the crystalline regions.

The above result differs slightly in some respects from previous work on low-density and cross-linked polyethylenes. As reported in that work[9,10], some methyl and ethyl short branches and cross-links can enter the crystalline regions as defects, whereas in the present work the DAM units and even the neighbouring $CH_2$ groups are excluded from the crystalline regions. Taking into account the difference in steric hindrance of side groups, such a difference is quite understandable.

It is noteworthy that in our previous work[5] on EDAM, we suggested a method for determining the minimum crystallizable ethylene sequence length. The method requires the important premise that the DAM units must lie outside the crystalline regions. However, at that stage, no experimental evidence for that premise was provided. Such uncertainty can now be satisfactorily dispelled by the above experimental result.

**Figure 2** 'Pure crystalline' $^{13}C$ spectrum of DA3002 obtained by using a Torchia pulse sequence

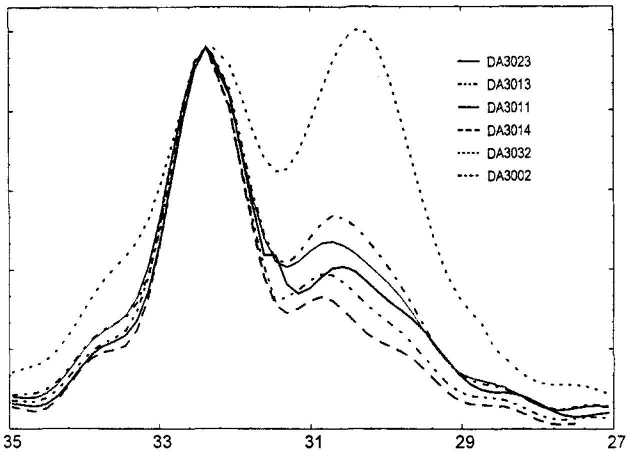


**Figure 3** $^{13}C$ CP–MAS signals of PE segment of six EDAM samples

*Phase structure and its relation to DAM content*

The relation between the degree of crystallinity and DAM content has been well established previously[4]. However, due to the existence of the interfacial phases and two types of crystals in EDAM samples, the degree of crystallinity can serve only as a rough measure of the phase structure. It is worth correlating the content of each phase component with the content of DAM comonomer. As shown in *Figure 1a*, $^{13}C$ CP–MAS signal of the ethylene segment consists of four peaks overlapping one another, corresponding to monoclinic crystals (M), orthorhombic crystals (O), interfacial region (I) and amorphous region (A). By peak simulation, the relative intensities of these four peaks can be assessed. Although the relative intensities obtained do not represent the real contents of these phase components in the samples, due to the non-quantitative nature of the CP technique, quantitative comparisons can be made of fitting results for samples with different comonomer contents. Accordingly, the influence of DAM content on the content of different phase components can be visualized.

*Figure 3* shows the $^{13}C$ CP–MAS signals of the PE segment of the six EDAM samples. The relative intensities of four peaks ($I_M$, $I_O$, $I_I$ and $I_A$, corresponding to the monoclinic, orthorhombic, interfacial and amorphous methylenes respectively) of each sample were obtained by computer-fitting and are listed in *Table 2*. The value of $I_M/I_O$, which is equivalent to the ratio of monoclinic to orthorhombic crystals, is plotted against the molar percentage of DAM in *Figure 4*. It is seen that $I_M/I_O$ increases linearly with increasing DAM content, while the degree of crystallinity decreases simultaneously. Our previous study[15] on the same series of copolymers by i.r. spectroscopy showed that the monoclinic crystalline structure occurs in both quenched and slowly cooled samples and its relative content also increases with increasing DAM content. All these results indicate that the content of comonomer unit influences not only the degree of crystallinity but also the structure of the crystalline region. Such a phenomenon in polyethylene copolymers has not yet been systematically studied.

The structure of an EDAM copolymer chain can be roughly described as many PE segments with different lengths connected by DAM units. It is reasonable to imagine that the crystallization behaviour of these PE segments

**Table 2** Computer-fitting results for $^{13}C$ CP–MAS signals of PE segment of six EDAM samples

| Sample | DAM content (mol%) | Phase composition (%) | | | |
|---|---|---|---|---|---|
| | | Monoclinic | Orthorhombic | Interfacial | Amorphous |
| DA3014 | 3.6 | 17.4 | 46.9 | 11.6 | 24.1 |
| DA3023 | 3.9[a] | 15.8 | 41.9 | 15.0 | 27.4 |
| DA3013 | 4.0 | 16.9 | 43.6 | 16.1 | 23.4 |
| DA3011 | 4.4 | 16.3 | 40.2 | 19.4 | 24.2 |
| DA3002 | 6.9 | 19.6 | 36.2 | 21.7 | 22.5 |
| DA3032 | 10.7 | 16.5 | 21.5 | 13.1 | 48.7 |

[a] Obtained by titrimetric analysis

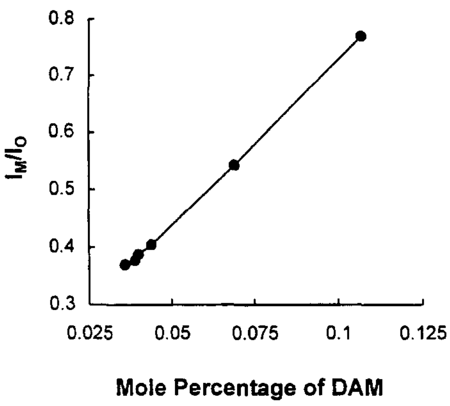


**Figure 4** Ratio of peak intensity of monoclinic crystalline methylenes to that of orthorhombic crystalline methylenes ($I_M/I_O$) *versus* molar percentage of DAM in EDAM samples

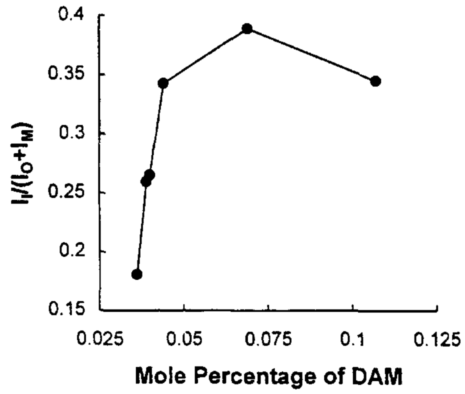


**Figure 5** Ratio of peak intensity of interfacial methylenes to that of crystalline methylenes [$I_I/(I_M + I_O)$] *versus* molar percentage of DAM in EDAM samples

varies with their length. For a relatively short PE segment, the DAM units on the two ends of the segment can greatly influence its flexibility and make it behave like cycloalkanes of small ring size in the crystallization process[16,17]. In such a case, the monoclinic form may be thermodynamically stable and/or dynamically favoured. On the other hand, for relatively long PE segments, the influence of DAM units may be small and these segments may behave like polyethylene homopolymers. In such a case, the orthorhombic structure may be the thermodynamically stable form and the monoclinic crystals may occur in some rapid crystallizing processes. From such considerations, it is easy to interpret the above experimental results. It is already known that the percentage of short polyethylene segments increases with increasing DAM content[5] and the monoclinic form is thermodynamically stable and/or dynamically favoured for relatively short PE segments; thus an increase in DAM content leads to an increase in the ratio $I_M/I_O$.

*Figure 5* plots the ratio of peak intensity of interfacial methylenes ($I_I$) to that of crystalline methylenes ($I_M + I_O$), $I_I/(I_M + I_O)$, against molar percentage of DAM. Although the contribution from DAM units and the neighbouring $\alpha$ and $\beta$ $CH_2$ groups which may also lie in the interfacial region is not included in $I_I$, the ratio $I_I/(I_M + I_O)$ can represent approximately the content of the interfacial component relative to that of the crystalline region. The interfacial component that is reflected in the $^{13}C$ CP–MAS spectrum may be associated with the crystalline–amorphous interface and some amorphous structures with restricted mobility, e.g. physical entanglements in the amorphous region. It can be seen from the plot that $I_I/(I_M + I_O)$ increases with increasing DAM content when the DAM content is $< 10$ mol%. This can be explained as follows. With increasing DAM content, the number-average ethylene sequence and hence the average crystal thickness decrease, whereas the thickness of the interface and the content of the above-mentioned amorphous structures with restricted mobility remain constant. Thus the content of the interfacial region relative to that of the crystalline region increases with the DAM content. Because the contribution of DAM units and the neighbouring $\alpha$ and $\beta$ $CH_2$ groups is not included in $I_I$ and the amount of these groups in the interfacial region may increase with increasing DAM content, the ratio $I_I/(I_M + I_O)$ decreases slightly when the DAM content reaches 10 mol%.

## CONCLUSIONS

A series of ethylene–dimethylaminoethyl methacrylate copolymers with different contents of DAM comonomer units have been studied by solid-state high-resolution $^{13}C$ n.m.r. spectroscopy. It has been found that both the DAM units and the $\alpha$ and $\beta$ methylene units relative to the tertiary carbon of DAM lie outside the crystalline region. Computer-fitting of the $^{13}C$ CP–MAS signals of ethylene sequences reveals that the fractional ratio of monoclinic crystals to orthorhombic crystals and the ratio of interfacial region to crystalline region increase with increasing DAM content. These results indicate that the crystallization behaviour and the phase structure of EDAM copolymers are closely associated with the chain structure.

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