ELSEVIER

S0032-3861(96)00616-7

Polymer Vol. 38 No. 5, pp. 1203–1205, 1997

0032-3861/97/$17.00 + 0.00

Influence of the sequence distribution on the crystalline structure of ethylene–dimethylaminoethylmethacrylate copolymers

Qun Chen*, Huijun Luo and Guang Yang
Analytical Center, East China Normal University, Shanghai 200062, China

and Duanfu Xu
Institute of Chemistry, Academia Sinica, Beijing 100080, China
(Received 13 February 1996; revised 27 May 1996)

The comonomer sequence distributions of a series of ethylene–dimethylaminoethylmethacrylate copolymers (EDAM) were measured by quantitative high-resolution ^{13}C n.m.r. spectroscopy. It was found that both the crystallinity and the lamellar thickness of EDAM samples increase linearly with the increase of the numerical average sequence length of ethylene run. It was further demonstrated that only ethylene longer than a critical length can participate in crystallization. Such a critical length was found to be independent of the molecular weight and composition of EDAM samples under the same crystallization condition. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: comonomer sequence distribution of copolymer; crystalline structure; high-resolution ^{13}C n.m.r.)

INTRODUCTION

EDAM, which is copolymerized with ethylene and *N,N'*-dimethylaminoethylmethacrylate (DAM) by high-pressure radical polymerization, has received attention from polymer physicists for nearly thirty years because of its commercial and scientific importance[1–3]. Recently, the molecular characteristics and crystalline structures of a series of EDAM copolymers were studied extensively[4] and related to macroscopic properties such as the melt-point T_m and the heat of fusion ΔH_f of the materials. Various kinds of techniques including SAXS, WAXD, d.s.c., TEM, i.r. were employed. The comonomer sequence distributions of two samples were also determined with 1D and 2D n.m.r. spectroscopy. However, the influence of the microstructure of the copolymer chain on the crystalline structure remains uninvestigated. In this work, the comonomer sequence distributions of four samples from the same series of EDAM copolymers have been measured by high-resolution ^{13}C n.m.r. Efforts have been made to establish the relationship between the chain structure (e.g. the comonomer sequence distribution and the numerical average ethylene chain length) and the crystalline structure of the copolymers[5].

EXPERIMENTAL

Quantitative high-resolution ^{13}C n.m.r. measurements were carried out on a Bruker AMX-400 spectrometer operating at 100.61 MHz with an inverse gated decoupling pulse sequence at 60°C. Four EDAM samples, named DA3011, DA3013, DA3014 and DA3002, were measured. The solvent was deutero-chloroform. The pulse interval was 10 s and the number of accumulations about 10 000. Peak assignments were made according to Ohmae's procedure[4]. The monomer compositions of EDAM samples were determined from n.m.r. data and the results were in good agreement with those determined by titrimetric analysis. *Table 1* lists the weight fraction of DAM monomer, the number-average molecular weight (M_n), the crystallinities (X_c) and the lamellar thickness (L_c) of the samples.

RESULTS AND DISCUSSION

From the ^{13}C n.m.r. peak intensities of the alkane region, the monomer composition, together with the diad and triad sequence distributions of EDAM copolymers, can be calculated according to Ohmae's procedure[4]. The results are listed in *Table 2*, in which E and M represent ethylene and DAM respectively. Data for DA1701 and DA3032 in *Table 2* were determined by Ohmae *et al.* From these data, the numerical average sequence lengths of ethylene run (L_e, counted with CH_2CH_2 unit) were calculated[4,7] and also listed in *Table 2*. Variations of X_c and L_c of the samples with L_e are shown in *Figures 1* and *2*. It can be seen clearly that both the crystallinity and the lamellar thickness vary linearly with L_e. Such a result suggests that the comonomer sequence distribution plays a more important role in determining the crystalline structure of EDAM copolymers than other structural factors such as DAM content, molecular weight or molecular weight distribution.

By comparing the data of comonomer sequence distribution obtained from ^{13}C n.m.r. with those simulated with probability theory, Ohmae *et al.*[4] demonstrated in their work that EDAM copolymers satisfy the complete

---

* To whom correspondence should be addressed

mixing continuous flow model. They found that the chain propagation of EDAM copolymer can be well described by the stationary first-order Markov process. Our results listed in *Table 1* also support such a conclusion. Therefore, through numerical calculation based on the ^{13}C n.m.r. data, we can obtain the molar percentage, $f(n)$, of the ethylene runs with a certain length n in all kinds of ethylene runs[6,7], which allows further analysis of the influence of the comonomer sequence distribution on crystalline structures. $f(n)$ is given by:

$$f(n) = P_{11}^{n-1}P_{12} \tag{1}$$

where P_{11} and P_{12} represent the conditional probabilities and 1 and 2 represent the ethylene unit and the DAM unit respectively. P_{11} and P_{12} were calculated from n.m.r. data and are listed in *Table 2*.

It is easy to visualize that there exists a minimum length n_0 (counted with CH_2CH_2) such that only ethylene runs longer than n_0 can participate in crystallization. However, the crystallinity of ethylene runs longer than n_0 cannot be 100% because of: (1) dynamic factors in the sample crystallization process; (2) ethylene chain-folding and steric hindrance of the DAM units. Let $X_{c'}$ represent the weight percentage of ethylene runs located in the crystalline region in the total of ethylene runs longer than n_0. The following equation can be easily derived:

$$X_c = \frac{X_{c'} \sum_{n\geq n_0}^{\infty} nf(n)}{\sum_{1}^{\infty} nf(n)} PE\% \tag{2}$$

where $PE\%$ represents the overall weight fraction of ethylene monomer in the copolymer. Then we have:

$$X_{c'} = \frac{X_c \sum_{1}^{\infty} nf(n)}{PE\% \sum_{n\geq n_0}^{\infty} nf(n)} \tag{3}$$

Thus, for each EDAM sample listed in *Table 2*, we can obtain a plot of $X_{c'}$ against n_0 through numerical calculation (*Figure 3*). We make the assumption here that, under the same crystallization condition, these samples should exhibit the same $X_{c'}$ and n_0. If such an assumption is correct, curves of $X_{c'}$ against n_0 should converge. From *Figure 3*, it is clear that five curves almost intersect at the same point, the only exception being the curve for DA3032. Such an exception may be caused by the relatively larger measurement error of the crystallinity of DA3032 which is the smallest of those of the EDAM samples, or the above assumption is valid only when the DAM content falls in a certain range. The above result suggests that EDAM samples with different DAM contents and different molecular weights may have the same n_0 and $X_{c'}$ under the same crystallization

Table 1 Characteristics of EDAM copolymer samples

Samples	DAM content (wt%)	M_n $\times 10^{-4}$	X_c (wt%)	L_c (Å)
DA3014	17.3[a]	7.80	44.3	76
DA3013	19.1[a]	2.94	40.5	67
DA3011	20.4[a]	2.64	38.6	61
DA1701	26.7	2.84	27.8	42
DA3002	29.4[a]	1.50	22.7	34
DA3032	40.1	3.37	14.5	24

[a] The unmarked data were reported by Ohmae *et al.*[4]

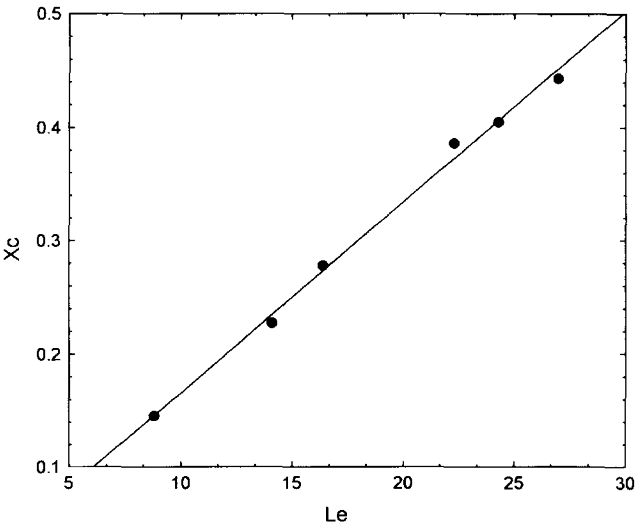

Figure 1 Crystallinity (X_c) as a function of the numerical average sequence length of ethylene run (L_c) of EDAM copolymers

Table 2 Data of sequence distributions, conditional probabilities and numerical average sequence lengths of ethylene run (L_c) of EDAM copolymers

	DA3011	DA3013	DA3014	DA3002	DA1701[a]	DA3032[a]
E	0.96	0.96	0.96	0.93	0.94	0.89
M	0.04	0.04	0.04	0.07	0.06	0.11
EE	0.91	0.92	0.93	0.86	0.88	0.79
EM	0.086	0.079	0.071	0.13	0.11	0.20
MM	0.0007	0.0007	0.0004	0.0032	0.0024	0.0053
EEE	0.88	0.89	0.90	0.81	0.83	0.68
EEM	0.080	0.036	0.068	0.12	0.11	0.18
EME	0.037	0.035	0.032	0.058	0.058	0.12
MEM	0.0040	0.0033	0.0022	0.0033	0.0045	0.010
MME	0.0014	0.0014	0.0008	0.0064	0.0024	0.0051
MMM	0.00	0.00	0.00	0.00	0.00	0.00
P_{11}	0.96	0.96	0.96	0.93	0.94	0.89
P_{12}	0.045	0.041	0.037	0.071	0.061	0.11
L_c	22.32	24.27	27.17	14.10	16.40	8.81

[a] Data for DA1701 and DA3032 were reported by Ohmae *et al.*[4]

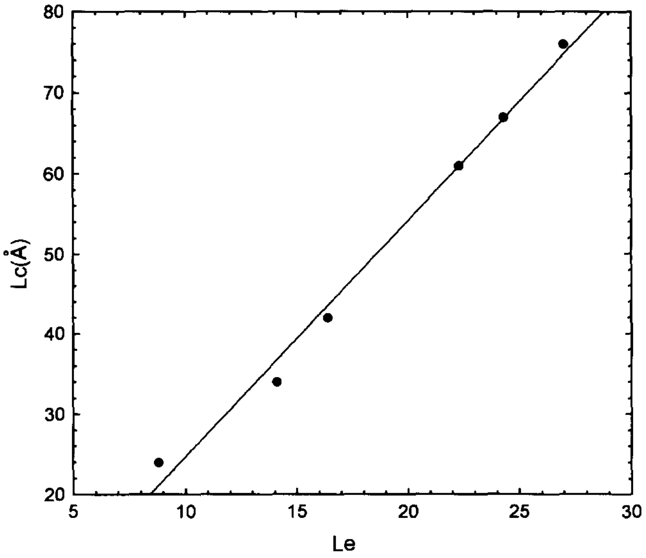

Figure 2 Lamellar thickness (L_c) as a function of the numerical average sequence length of ethylene run (L_e) of EDAM copolymers

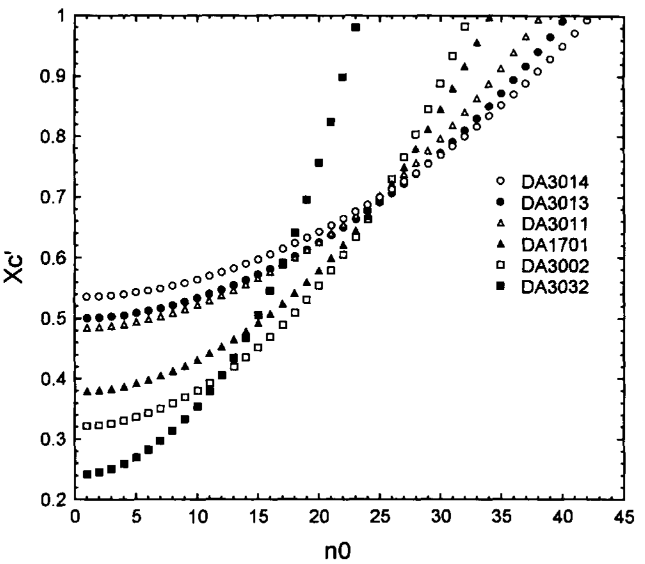

Figure 3 Plots of $X_{c'}$ vs n_0 obtained by numerical calculation according to equation (3)

conditions. The n_0 and $X_{c'}$ obtained from the cross-point in *Figure 3* are 25 and 70% respectively. Although the branching of EDAM copolymer chains may affect the molar percentage $f(n)$ and the average sequence length of ethylene run, it was ignored in the above data processing because of the low degree of branching as revealed by the n.m.r. spectra.

The value of n_0 we believe, can be related to the least lamellar thickness of ethylene crystal. Our recent work[8] on the same series of EDAM samples with solid-state high-resolution ^{13}C n.m.r. spectroscopy reveals that almost all DAM units together with the α and β CH_2 units adjacent to the tertiary carbon of DAM, locate in the noncrystalline region. Therefore, for the smallest ethylene run that can participate in crystallization, the largest length that locates in the crystalline region should be 23 (counted with CH_2CH_2), instead of 25. The thickness of the corresponding lamella should be about 52 Å if the ethylene chain takes all *trans* conformation. This result is in good agreement with the least lamellar thickness (30 ~ 40 Å) observed by Xu *et al.* by TEM on the same series of EDAM samples[9].

The fact that five samples exhibit the same value of $X_{c'}$ may suggest that the ethylene run behaves like a pure ethylene chain in the crystallization process when its length is longer than n_0. Such a value may depend on the crystallization condition and may hold more information about the chain-folding than the crystallinity in its common meaning does. The above results have revealed how crystalline structures are influenced by the sequence distribution. Therefore they are quite important for understanding the crystallization mechanism and the relationship between chain structures and crystalline structures of EDAM copolymers. It is interesting to apply the above method to studying the variance of n_0 and $X_{c'}$ with crystallization condition or to other crystalline copolymer systems. Further research according to the above strategy is continuing.

CONCLUSIONS

The comonomer sequence distribution of EDAM copolymers was studied by high-resolution ^{13}C n.m.r. spectroscopy and related to the crystalline structures obtained from SAXS and WAXD measurements. The following conclusions can be drawn.

(1) Both the crystallinity and the lamellar thickness of the copolymers increase linearly with increase of the numerical average length of ethylene runs, indicating that the comonomer sequence distribution has great influence on the crystalline structure of the copolymers.

(2) By numerical calculation based on the data of comonomer sequence distribution, crystallinity and overall weight fraction of ethylene monomer in copolymers, it was demonstrated that five samples exhibit the same n_0 and $X_{c'}$. The values of n_0 and $X_{c'}$ were determined for the first time. The least lamellar thickness estimated from n_0 is in good agreement with TEM observations.

ACKNOWLEDGEMENTS

This work was supported by the National Foundation of Natural Science of China, the Shuguang Project of Shanghai Education Committee and Polymer Physics Laboratory, Academia Sinica. The authors are indebted to Mr X. M. Kong of Shanghai Institute of Petroleum Chemical Industry for n.m.r. measurements.

REFERENCES

1 Tatsukami, Y. *J. Chem. Soc. Japan* 1978, **12,** 1696
2 Taniguchi, I., Maemoto, K., Tatsukami, Y. and Kobayashi, Y. *US Patent 3 653 803,* 1968
3 Ohmae, T., Yamaguchi, N., Konde, A. and Okada, T. *US Patent 4 721 761,* 1988
4 Ohmae, T., Hosoda, S., Tanaka, H., Kihara, H., Jiang, B., Ying, Q., Qian, R., Masuda, T. and Nakajima, A. *Pure Appl. Chem.* 1993, **65,** 1825
5 Chen, Q., Luo, H. J., Yang, G. and Xu, D. F. *Chin. J. Polym. Sci.* (submitted as rapid communication)
6 Coleman, B. D. and Fox, T. G. *J. Polym. Sci.* 1963, **A1,** 3183
7 Bovey, F. A. 'Chain Structure and Conformation of Macromolecules', Academic Press, New York, 1982
8 Luo, H. J., Chen, Q., Yang, G. and Xu, D. F. (in preparation)
9 Zhang, H. P. and Xu, D. F. (unpublished data)