Macromolecules **1992,** *25,* 2277-2279

New Crystalline Conformer in Poly(*N*-acylethylenimine) Copolymers Containing Pendant Pentamethyldisiloxanyl Groups

Gangfeng Cai and Morton H. Litt*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

Received May 9, 1991
Revised Manuscript Received January 12, 1992

Introduction

Recently, two series of random copolymers of [10-(pentamethyldisiloxanyl)decyl]oxazoline (Si) with undecyl- (U) and nonyloxazolines (N) with a total degree of polymerization of 100 over the whole composition range were made.[1] They were named N/Si(*m*/*n*) and U/Si(*m*/*n*), where *m* and *n* are the total number of N or U and Si monomer units, respectively. A DSC and wide-angle X-ray diffraction study[2] demonstrated that these random copolymers crystallized two dimensionally over a broad range of copolymer compositions from 10 up to 65 mol % (for N/Si) and from 10 to 50 mol % (for U/Si) of Si. Their wide-angle X-ray diffractograms all show 010, 020, and 030 reflections which correspond to long spacings of 24–34 Å depending on the mole fraction of Si in the copolymer.[2] In this paper, we report on a second set of reflections which were found in these copolymers after they were heated at 160 °C.

Experimental Section

Materials. The synthesis and characterization of random copolymers of [10-(pentamethyldisiloxanyl)decyl]oxazoline (Si) with nonyl- (N) and undecyloxazolines (U) over the whole composition range, and with an approximate degree of polymerization of 100, have been reported previously.[1,2]

Film Preparation and Wide-Angle X-ray Diffraction. Thick films were cast onto glass slides from 20 wt % solutions of the polymers in chloroform. After drying, they were held at about 160 °C for 30 min or in some cases for 3 h in a vacuum oven. The oven power was turned off, and the samples cooled to room temperature in about 3 h. X-ray scans were performed using a Philips APD 3520 automatic diffractometer with nickel-filtered Cu Kα radiation. Scans were run from 1° to 32° with a goniometer speed of 1.2°/min.

Results and Discussion

2-Alkyl-substituted oxazolines polymerize cationically to form poly(*N*-acylethylenimines). In general, such polymers tend to crystallize easily. As was shown for this case, even random copolymers with acyl side chains can crystallize well. Litt et al.[3] showed that such polymers crystallized with the C–C backbone in the trans conformation with side chains alternating 180° around the backbone. The chain repeat of two monomer units was 6.3–6.4 Å. The side-chain spacings depended, of course, on the side-chain length and showed that the alkyl chains were tilted about 36° from the normal to the backbone.

When these polymers were melted (at $T_m + 10$ °C) and allowed to crystallize slowly, a series of low-angle peaks relating to the polymer side-chain spacings were seen.[2] Their *d*-spacings depended on the monomer (N or U) and on the mole fraction of Si in the copolymers. After the N/Si copolymers with a mole percentage of Si from 20 to 90% were heated at 160 °C for 30 min or more, a second set of low-angle reflection peaks appeared in addition to those discussed before[2] (Figure 1 and Table I). This set of reflections was much sharper than the first set of peaks. N/Si(70/30) had the strongest second set of peaks. For N/Si(90/10), the second set of peaks was seen only after long heating (about 30 h at 160 °C; Figure 2). No second set of peaks was seen in N/Si(95/5), Si, and N homopolymers. The average long spacings calculated from this set of peaks ranged from 41 to 43 Å and barely changed with copolymer composition, within experimental error (Figure 3). Under the conditions at which the second set of reflections was generated, the polymers became lightly cross-linked. Two U/Si copolymers (U/Si(74/20) and U/Si(59/57)) were also studied and showed a similar second set of peaks.

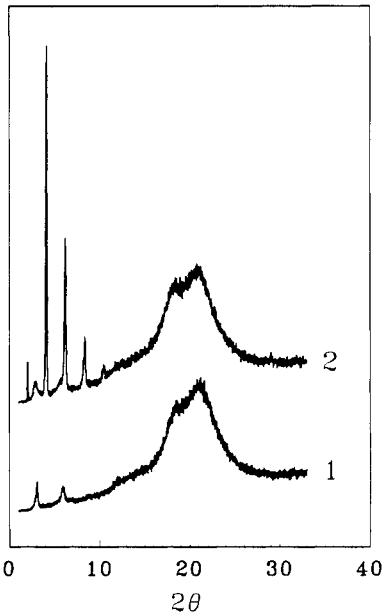

Figure 1. Wide-angle X-ray diffraction spectra of N/Si(70/30) copolymer films coated on glass slides. (1) The sample was heated to 145 °C and cooled to room temperature in about 20 min. (2) The sample was heated to 160 °C, held for 30 min, and slowly cooled to room temperature (3 h).

As mentioned before, early studies[3] demonstrated that poly(*N*-acylethylenimine) polymers with linear acyl side chains contained two monomer units per repeat; the main-chain carbon atoms had a trans dihedral angle conformation with the acyl side chains fully extended and alternating around the backbone, tilted approximately 36° from the perpendicular to the chain axis. The side-chain dimension of the unit cell (the 010 spacing) ranged from 11.6 Å for *n*-butyryl to 28 Å for *n*-dodecanoyl side chains. The maximum long spacing for the N/Si copolymers was found to be 34 Å;[2] the calculated long spacing for the Si polymer with the side chain tilted at 36° to the normal to the backbone was also 34 Å. The second set of peaks, with a long spacing of 42 ± 1 Å, implies that there must be a second type of packing and/or conformation in which the side chains are no longer tilted, or at least much less tilted. Poly(*N*-acylethylenimine)s with bulky carbazole derivatives attached to their polymethylene side chains were found to crystallize with a gauche backbone conformation with the side chains alternating on each side of the backbone and perpendicular to its axis.[4] Conformational calculations showed that the chain repeat (two monomer units) was about 4.5–4.8 Å. With such a packing structure,

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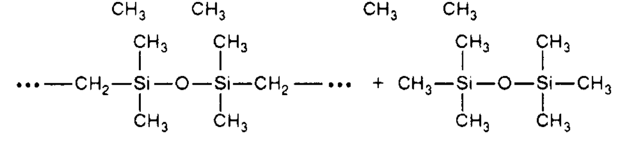
Table I
Second Sets of *d*-Spacings of the X-ray Diffractions of N/Si and U/Si Random Copolymers

polymer	2θ	*d*-spacing, Å	weighted average long spacing, Å
N/Si(90/10)	2.04	43.3	43.5 ± 0.2
	4.04	21.88	
	6.08	14.56	
	8.17	10.85	
	10.24	8.67	
N/Si(80/20)	2.09	42.3	41.9 ± 0.3
	4.18	21.15	
	6.39	13.85	
	8.50	10.43	
	10.59	8.39	
N/Si(70/30)	2.05	43.1	42.6 ± 0.2
	4.12	21.46	
	6.24	14.18	
	8.36	10.60	
	10.45	8.50	
N/Si(50/50)	2.13	41.5	42.4 ± 0.3
	4.20	21.05	
	6.28	14.09	
	8.34	10.63	
	10.40	8.54	
N/Si(35/65)	2.16	40.9	41.0 ± 0.1
	4.30	20.56	
	6.50	13.62	
	8.65	10.25	
N/Si(20/80)	2.22	39.8	40.4 ± 0.6
	4.30	20.56	
	6.63	13.35	
N/Si(8/83)	2.20	40.2	40.7 ± 0.4
	4.30	20.56	
	6.55	13.52	
U/Si(74/20)	2.06	42.9	42.7 ± 0.3
	4.10	21.56	
	6.18	14.32	
	8.34	10.63	
	10.44	8.51	
U/Si(59/57)	2.12	41.7	42.4 ± 0.3
	4.20	21.05	
	6.28	14.09	
	8.34	10.64	
	10.40	8.54	

the calculated long spacing for the N/Si copolymer is approximately 42 Å, which agrees with the experimental long spacing of 42 Å. As expected, both U/Si(74/20) and U/Si(59/57) have the same average long spacings within experimental error (Table I). We propose, therefore, that heating generated a second conformer with the side chain perpendicular to the main chain, with a carbon–carbon gauche conformation along the backbone.

It was found that the copolymers were lightly cross-linked after being heated at 160 °C. The homopolymer of N or U does not cross-link. The cross-linking is probably due to the reaction between the disiloxanyl tails, as shown in the following:



$$\cdots-CH_2-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3 + CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2-\cdots \longrightarrow$$

$$\cdots-CH_2-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2-\cdots + CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

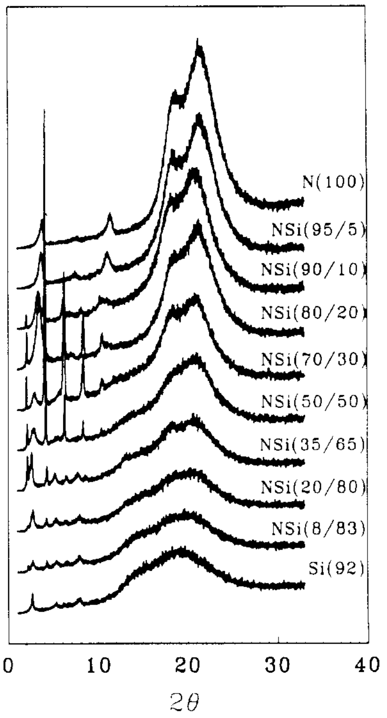


Figure 2. Wide-angle X-ray diffraction spectra of the N/Si copolymer films after they were held at 160 °C.

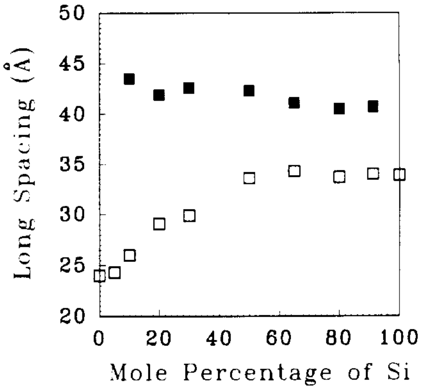


Figure 3. Post 160 °C heating relationships between the mole percentage of the Si monomer in the N/Si copolymers and their average long spacings: (□) Average long spacings calculated from the first set of diffraction peaks. (■) Average long spacings calculated from the set of diffraction peaks generated after heating.

This was confirmed by the loss of silicon in N/Si(70/30) after heating. The concentration of Si^5 in N/Si(70/30) decreased from 7.40% (0.33 mole fraction of Si) to 6.56% after being heated at 160 °C for 30 min. This is equivalent to reaction of about 28% of the disiloxanyl tails, 9% of all the tails. If all this reaction produced cross-links, the polymer should be highly cross-linked. However, it swelled greatly in solvent, showing that it was only lightly cross-linked. Most of the reaction must have been intramolecular. Simple calculations show that about 50% of the Si units are adjacent to other Si units and thus could have reacted to generate intramolecular links.

The reaction between disiloxanyl groups in two polymer chains should cross-link the polymer. Reaction between disiloxanyl groups in neighboring side chains along the same backbone should generate a >SiOSi< linkage with a distance of about 4.5 Å.[6] Such a link would prevent the polymer from adopting its normal conformation when it crystallizes, since that chain repeat is 6.3 Å.[3] However, the repeat with the gauche conformer backbone is about 4.5 Å. Thus, when the polymer melts were cooled, this linkage possibly forced the polymers to crystallize with the gauche backbone conformation. Calculations showed that both conformers have almost equal energy for poly(*N*-hexanoylethylenimine).[4] While the Si homopolymer and the N/Si(8/83) copolymer cross-link, they do not form the extended structure. This is probably due to the large size of the pentamethyldisiloxanyl groups attached to the alkyl chains which forces the side chains further apart than 4.5 Å and prevents the crystallization. In fact, the Si homopolymer, Si(92), showed no second set of peaks even after being heated at 160 °C for 3 h. In the copolymers containing less than 20 mol % of Si, the probability of two disiloxanyl groups adjacent to each other is low. Therefore, it is difficult to generate the gauche backbone conformation in these polymers.

Acknowledgment. We gratefully acknowledge financial support from the Center for Adhesives, Sealants and Coatings, Case Western Reserve University, Cleveland, OH.

References and Notes

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