Molecular Aggregation in Poly(vinyl Chloride). III. Role of Molecular Structure

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Synopsis

The present study offers a visualization of the process of molecular aggregation in PVC polymerized at low temperatures in bulk. "Kinks" along with the chains are responsible for molecular entanglement with subsequent microcrystallization of the syndiotactic sequences. The crystallites act as bonding nuclei. The "kinks" are the result of the different chain conformations of isotactic and syndiotactic sequences. The number of "kinks" increases on lowering the polymerization temperature both because the chains are longer and also because of the more frequent switching between isotactic and syndiotactic placements.

INTRODUCTION

The presence of molecular aggregates in poly(vinyl chloride) was first discovered almost two decades ago by Doty and co-workers.[1] Later this was confirmed by other investigators[2-6] who observed some anomalies in dilute PVC solution properties. These anomalies were attributed to the presence of supermolecular structures. The size of these entities was estimated from light scattering measurements to be about 2500 Å and the molecular weight to be about 10^8. Using other measuring techniques, Hengstenberg and Schuch[7] concluded that these aggregates are about 140–180 Å in diameter and 11–25 times the size of a single molecule.

The aggregates in dilute solutions of PVC in THF or cyclohexanone were found to disintegrate very slowly into single molecules upon aging.[8] The disintegration process can be significantly accelerated by heating the solutions[9,10] or by applying ultrasonic waves.[11] Aggregates in PVC made at very low temperatures (less than −10°C) can only be disintegrated by severe heating for prolonged periods of time.[12]

The presence of aggregates does not only lead to errors in molecular weight measurements[2-4] but also affects the rheological properties of PVC melts.[13]

It was found experimentally[12] that the aggregate content, size, and stability increase at lower polymerization temperatures. Since syndiotacticity also increases with decreasing polymerization temperature, aggregation was successfully correlated with syndiotacticity.[10]

Lyngaae-Jorgensen[14] proposed a structural model of the aggregate which assumes that it is a star-branched polymer with approximately 24 long branches of random length held together by a crystalline nucleus.

The present article, which is the third in a series about molecular aggregation in PVC, is an extension of that model with an attempt to explain how these crystalline nuclei are formed and why aggregates made at different temperatures have different sizes and different stabilities.

EXPERIMENTAL

PVC samples were prepared in bulk in the temperature range of 30° to 70°C using chemical initiation (AIBN).

Low-temperature PVC samples (−10°C, −30°C, −50°C) were polymerized in bulk using γ-ray initiation and were supplied by G. Palma, Laboratorio di Fotochimica e Radiazioni d'alta Energia C.N.R., Padova, Italy. Initiation involved a dose rate of 2.2 rad/sec giving conversions in the range of 78% to 90%.

Theory of Aggregate Formation

Bulk polymerization of vinyl chloride is a typical example of heterogeneous systems. The polymer is insoluble in its own monomer, and hence polymer molecules precipitate out as soon as they are formed. For aggregation to take place, several molecules must be tied up together through a relatively strong nucleus such as a crystallite. Crystallites result from local microcrystallization of the syndiotactic sequences in the chains. To provide ample time for
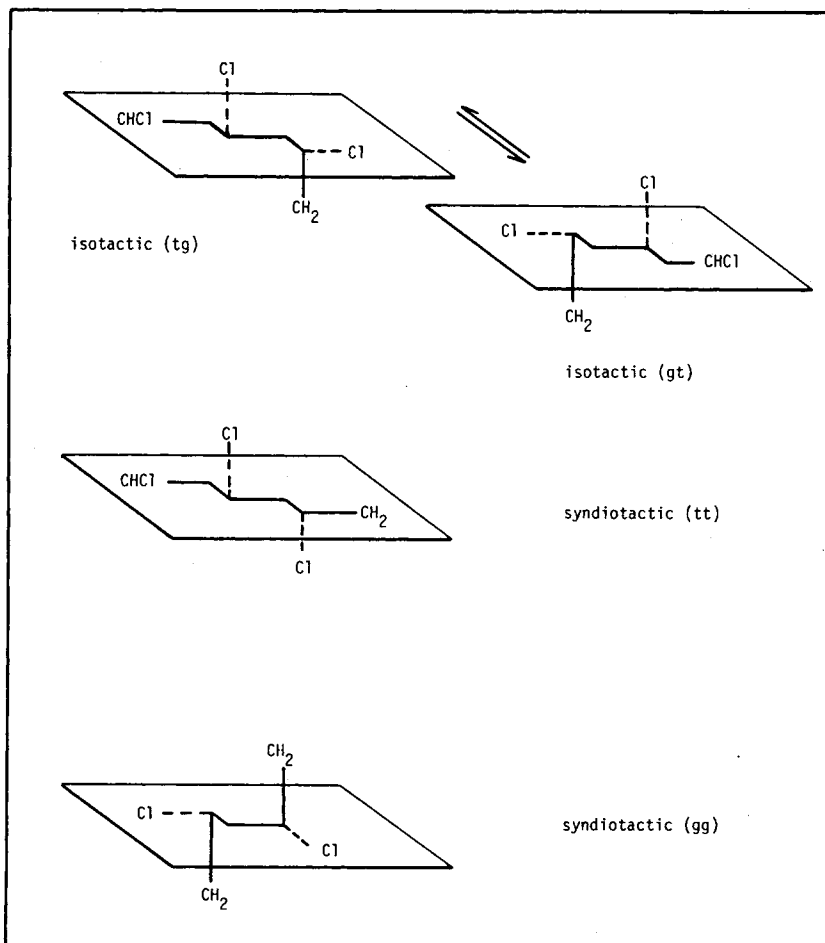

Fig. 1. Isotactic and syndiotactic conformations in PVC.

the crystallites to form the molecules must be entangled so that syndiotactic sequences are forced to remain in close contact for some time.

In their conformational study of PVC, Heatley and Bovey[15] showed that an isotactic diad interconverts rapidly between the two equivalent forms "tg" and "gt", where t is the "trans" and g the "gauche" structure of the repeating unit in the chain. This interconversion is shown in Figure 1, where the structures are represented schematically. The main chain is shown in solid line while the chlorine–carbon bonds are shown in dashed lines. When these conformations are repeated the 3_1 helix is generated. On the other hand, the syndiotactic diads have been shown[16–18] to exist mainly in the form "tt" and only to very small extent in the form "gg" (Fig. 1). When the structure "tt" is repeated, the familiar planar zigzag is generated. Since isotactic and syndiotactic sequences have different spatial conformations, a "kink" in the chain will occur at the junction point where the regularity switches from isotactic to syndiotactic or vice versa.

It is conceivable that during propagation, growing chains get entangled at the kink locations. Syndiotactic sequences of the entangled molecules may then align themselves to form crystallites. The crystallites act as bonding nuclei for the aggregates.

The average number of kinks along the chain (J) can be estimated as follows: If S is the diad syndiotacticity and I the diad isotacticity, it can be shown[19] that

$$\overline{N}_S = 2S/h = \rho_i/I = \rho_i/(1 - S)$$

and

$$\overline{N}_I = 2I/h = \rho_i/S \tag{1}$$

where $\bar{N}_S$ and $\bar{N}_I$ are the average syndiotactic and isotactic sequence length, respectively, and h is the triad heterotacticity. ρ_i is defined as the persistence ratio[19] and is given by

$$\rho_i = 2IS/h. \tag{2}$$

It represents the deviation of the propagation statistics from the Bernoullian (random) case for which ρ_i is unity. ρ_i then is the ratio of the average tactic sequence length to the average tactic sequence length had the propagation been Bernoullian.

Since PVC is nearly atactic polymer ($I \simeq S$), the average regular sequence length regardless of the type of regularity ($\bar{N}$) is given by

$$\overline{N} = \frac{1}{2}(\overline{N}_S + \overline{N}_I) = \frac{\rho_i}{2}\left(\frac{1}{1 - S} + \frac{1}{S}\right) = \frac{\rho_i}{2S(1 - S)}$$

$$\text{average number of senquences} = \frac{\text{average chain length}}{\text{average sequence length}}$$

$$= \frac{\bar{r}_N}{\rho_i/2S(1 - S)} = \frac{2S(1 - S)}{\rho_i}\bar{r}_N \tag{3}$$

$$\text{average number of kinks} = J = \frac{2S}{\rho_i}(1 - S)\bar{r}_N - 1 \tag{4}$$

where $\bar{r}_N$ is the number-average chain length.

RESULTS AND DISCUSSION

In a previous study of the nuclear magnetic resonance of PVC,[20] the parameters ρ_i, η_S, and G were defined and calculated for a series of PVC samples polymerized in bulk in the temperature range of 70°C to −50°C:

$$\eta_S = s/S^2 \tag{5}$$

$$G = h^2/4si \tag{6}$$

where s, i, and h are the triad syndiotacticity, isotacticity, and heterotacticity, respectively. These parameters, called the persistence ratios, can be looked upon as indicators of the pattern of regular propagation in the polymer chain. A value of unity indicates Bernoullian or random case. The opposite is true for ρ_i and η_s more than one or G less than one where there is a tendency to form stereoblocks and less frequent switching between isotactic and syndiotactic configurations. Table I shows the variation of the different persistence ratios with polymerization temperature for poly(vinyl chloride).[20] At lower polymerization temperatures, there is an increasing tendency to switch more often between isotactic and syndiotactic placements. Accord-

TABLE I
Variation of Molecular Properties of Bulk PVC with Polymerization Temperature

Polymerization temperature, °C	S	$\bar{r}_N$	ρ_i	η_s	G	J	A, %
70	0.544	400	1.04	1.03	0.848	189	—
50	0.559	816	1.02	1.02	0.913	393	—
45	0.565	954	1.01	1.01	0.971	462	1.2
40	0.568	1120	1.01	1.01	0.945	544	2.5
35	0.570	1300	0.988	0.991	1.05	644	3.9
30	0.576	1620	0.993	0.995	1.04	796	10.9
−10	0.615	7376	0.951	0.968	1.32	3672	78.5
−30	0.647	7520	0.906	0.944	1.60	3790	82.8
−50	0.673	7600	0.884	0.936	1.89	3783	87.1

Nomenclature

J	average number of kinks in the chain
S	diad syndiotacticity
I	diad isotacticity
$\bar{N}_S$	average syndiotactic sequence length
$\bar{N}_I$	average isotactic sequence length
$\bar{N}$	average sequence length
$\bar{r}_N$	number-average chain length
A	aggregate content
G	persistence ratio, eq. (6)
s	triad syndiotacticity
i	triad isotacticity
h	triad heterotacticity

Greek Symbols

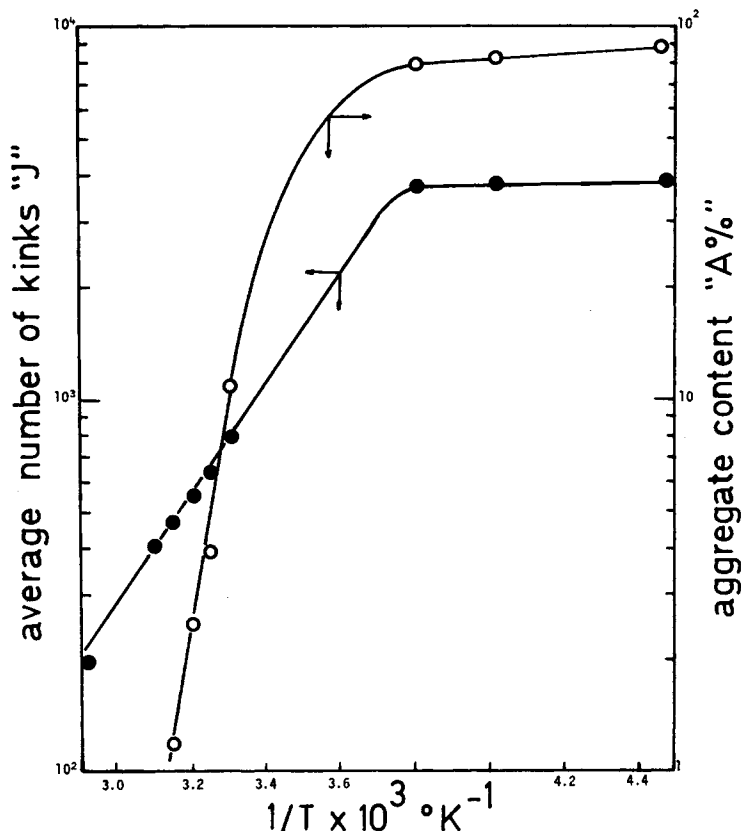| ρ_i, η_s	persistence ratios, eqs. (2) and (5)

Fig. 2. Variation of molecular properties of bulk PVC with polymerization temperature.

ingly, the average tactic sequences will be shorter and the average number of kinks will be higher than the corresponding Bernoullian case.

A similar study[21] has shown that in poly(methyl methacrylate) (PMMA) stereoblocks are formed at low polymerization temperatures as indicated by ρ_i and η_s more than one and G less than one at such temperatures.

The average number of kinks, J, was calculated for the PVC samples. Results are shown in Table I along with the aggregate content (A%) measured by GPC.[10,12] The number-average chain length ($\bar{r}_N$) and syndiotacticity (S) were extracted from reference 22. In Figure 2, the average number of kinks, J, and the aggregate content, A, in PVC are plotted versus polymerization temperature. The two curves have almost the same shape, which suggests the validity of the hypothesis that aggregation is enhanced by increasing the number of kinks. It should be noticed, however, that the increase in the number of kinks, J, is governed by the increase in the chain length. The contribution of the frequent alternation of tactic placements to the increased number of kinks at low polymerization temperatures is only minimal, nevertheless in the same direction. There are more kinks in the chains at lower polymerization temperatures primarily because the chains are longer at these temperatures.

The aggregation process can be visualized as follows: the key factor seems

to be the ability of the molecules to entangle with each other, with subsequent formation of crystallites. The syndiotactic sequences of the entangled molecules being able to crystallize[23] can undergo local microcrystallization. The extent of microcrystallization depends on polymerization temperature. Crystallites are thus formed in different locations in the polymer matrix. Depending on the size of these crystallites they can tie up different numbers of single molecules. Smaller crystallites made up of relatively shorter syndiotactic sequences are not very strong and hold only few molecules. When a solvent such as THF is added to the solid polymer, the three-dimensional matrix is disturbed by the penetration of the solvent molecules. The untied single molecular chains are the first to go into solution. Chains held by smaller crystallites may be freed by the solvent action. Depending on the solvent power and the dissolution temperature, some crystallites will not be penetrated by solvent molecules, and an aggregate of molecules held by a crystalline nucleus (or more) will remain as such. This was observed clearly in electron microscope photographs of PVC fractions insoluble in THF at room temperature.[12] Only prolonged heating of the solutions at elevated temperatures will disintegrate these aggregates.

At low polymerization temperatures, the molecules have more kinks in them, both because they are long and because of the frequent switching between isotactic and syndiotactic placements. It is thus expected that the aggregate content, size, and stability should increase with decreasing polymerization temperature.

This explains the absence of aggregates in solutions of PVC polymerized at higher temperatures such as 50° and 70°C. Solutions of PVC made at yet lower temperatures contain an increasing amount of aggregates, but these aggregates are generally small in size (2500 Å) and relatively unstable. They can be easily disintegrated by simple heating at 100°C for 10 min.[10,12] At very low polymerization temperatures (e.g., −50°C) the aggregate content is very high, and the aggregates themselves are large (5000 Å) and very stable. They disintegrate only after heating at 200°C for about 2 hr.[12]

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