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Change of the persistence lengths in the conformational transitions of pullulan- and amylose-tricarbanilates

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Introduction

It is well known that cellulose-tricarbanilate CTC and amylose-tricarbanilate ATC exhibit thermal-induced conformational transition from expanded form at low temperature to compact form at high temperature. It was suggested that intramolecular hydrogen-bonds formed between carbanilate groups neighboring along the backbone chain might be an origin for the conformational transition. In this study, the persistence length P_l of pullulan-tricarbanilate PTC and ATC in 1,4-dioxane DOX, N,N-dimethy formamide DMF and N-methyl acetylamide NMA solutions was evaluated at several temperatures with small-angle X-ray scattering SAXS and the temperature-dependence of the intrinsic viscosity [η] was analyzed with temperature-dependence of P_l thus obtained. PTC, ATC and CTC are discriminated from each other in the type of bonding joining the repeating units, and DMF and NMA would have facility of hydrogen-bond formation and thus affect or break intramolecular hydrogen-bonds in the polysaccharide-tricarbanilates.

Experimental

Materials: PTC, ATC and CTC were prepared by reaction of PL with phenyl isocyanate in hot pyridine (80-100ºC) [1]. Degree of substitution of phenylcarbanilate groups was 99.2%. Their viscosity-averaged molecular weight M_v was 2.1×10^5, 6.0×10^4, 5.1×10^4, respectively.

SAXS experiments: SAXS experiment was carried out at BL-10C in the Photon Factory of the High Energy Accelerator Organization at Tsukuba, Ibaragi, Japan. The details of the instrumentation and the procedure are described elsewhere [2]. The scattering intensity $I(q)$ was measured over a range of 0.01 to 0. 25 A^{-1} in q, where q is the magnitude of the scattering vector, defined by $(4\pi/\lambda)\sin(\theta/2)$, and λ is the wave length of X-ray and θ is a scattering angle.

Results and discussion

$I(q)$ was converted to scattered intensity $I_{thin}(q)$ for a hypothetical chain with null cross-section [1]. P_l was evaluated on the basis of $I_{thin}(q)$. As an example, Figure 1 shows the Kratky plot $I_{thin}(q)q^2$ vs. q for PTC: (A) 20C in DOX, Cp=0.69g/dl; (B) 40C in DOX, Cp=1.00g/dl and 0.50 g/dl; (C) 60C in DOX, Cp=0.69g/dl; (D) 20C in DMF, Cp=0.71g/dl; (E) 60C in DMF, Cp=0.71g/dl; (F) 40C in NMA, Cp=1.00g/dl and 0.50 g/dl. It is seen that the data in a high q range is well on a straight-line (solid line) passing through an origin, showing the q range is the Porod-region, but the data begins to deviate upward from the line as q is decreased. The transition point q^* (dotted line) between Debye-region and Porod region was assumed to be equal to q where the deviation appears. From the q^*, P_l was evaluated to be (A) 45±3A, (B) 44±3A, (C) 42±3A, (D) 41±3A, (E) 35±3A and (F) 30±3A. The data analysis with the particle scattering function for the wormlike chain has given the almost identical magnitudes of P_l for PTC.

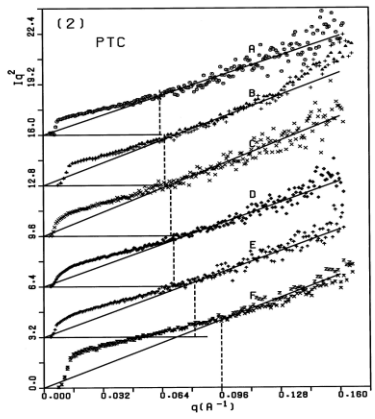

Fig.1 The Kratky plot for PTC.

In conclusion, the following was derived: The thermal-induced conformational transition for PTC and ATC is clarified from the temperature dependence of [η]. It was shown that P_l decreases as the conformational transition proceeds and the temperature dependence of [η] is well elucidated in terms of temperature-dependent P_l with the wormlike chain model. It is concluded that intramolecular hydrogen bonds would be formed between carbanilate groups neighboring along the backbone chain.

The detail of this study has been published [1].

References

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