

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Crystallinity in Free Radical Polymerized Polyvinyl p-t-butylbenzoate)

Maged A. Osman^a; Hans-Georg Elias^a

^a Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology at Zurich, Zurich, Switzerland

To cite this Article Osman, Maged A. and Elias, Hans-Georg(1971) 'Crystallinity in Free Radical Polymerized Polyvinyl p-t-butylbenzoate)', *Journal of Macromolecular Science, Part A*, 5: 4, 805 – 808

To link to this Article: DOI: 10.1080/00222337108061060

URL: <http://dx.doi.org/10.1080/00222337108061060>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LETTER TO THE EDITOR

Crystallinity in Free Radical Polymerized Poly(vinyl p-t-butylbenzoate)

Vinyl polymers prepared by free radical polymerization at elevated temperatures are in general noncrystalline materials. Notable exceptions are polymers obtained from vinyl compounds with relatively small substituents (e.g., polyvinyl alcohol, polyvinyl chloride) or with long straight chain substituents (polyvinyl stearate [1]). In this letter we want to report some observations of crystallinity in a free radical polymerized poly(vinyl ester) with a bulky substituent, poly(vinyl p-t-butylbenzoate).

Earlier observations on the silicon analog, poly(vinyl p-trimethylsilyl benzoate) have shown the existence of some crystallinity (DTA, x-ray, polarizing microscope) in a sample polymerized with α,α' -azobisisobutyronitrile at 70°C [2]. It was thus considered interesting to investigate the corresponding C-pendant, viz., poly(vinyl p-t-butyl benzoate). This polymer was said to have a glass transition temperature of 101°C [3] and a melting temperature was not reported.

Different poly(vinyl p-t-butylbenzoates) were prepared by bulk polymerization of the GC-pure monomer at 70°C using different amounts of α,α' -azobisisobutyronitrile as initiator. After two hr, the polymerization was stopped and the reaction mixture dissolved in benzene. The polymer was precipitated in methanol and dried at 50°C under vacuum.

The DTA's (Fig. 1) showed glass transition temperatures at 140°C, onset of crystallization, and melting points at 326°C followed by decomposition (Table 1). In the polarizing microscope, all four samples were found to be partially crystalline. X-ray diffraction failed to detect crystallinity in the two lower molecular weight Samples III and IV, but gave two sharp lines in the Debye-Scherrer diagram of the high molecular weight Samples I and II (Fig. 2).

Sample I was hydrolyzed and the PRS of the poly(vinyl alcohol) taken in D₂O at 39°C using a 100 MHz Varian apparatus. The α proton when decoupled from the β protons exhibited 3 components corresponding to

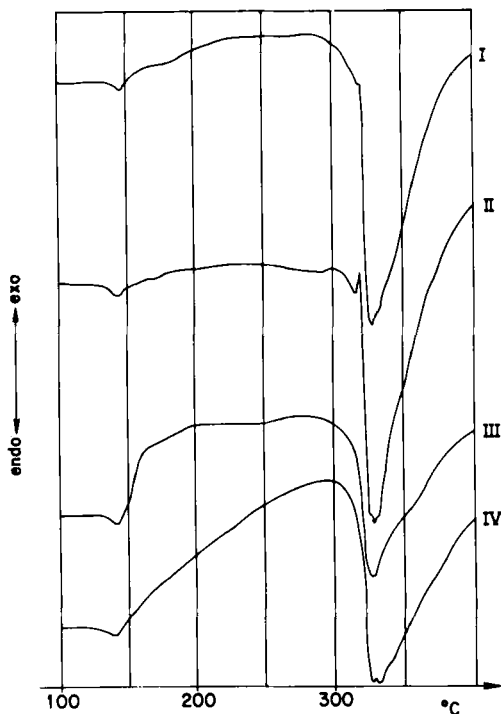


Fig. 1. DTA traces of poly(vinyl p-t-butylbenzoates); 19 mg samples, speed 20°C/min. (Symbols I-IV correspond to those given in Table 1).

Table 1. Weight-Average Molecular Weights M_w (Light Scattering, 25°C, Toluene), Intrinsic Viscosities $[\eta]$ (25°C, Toluene), Glass Transition Temperatures T_g , and Melting Points T_m (both DTA) of Poly(vinyl p-t-Butylbenzoates) Prepared in Bulk at 70°C Using Different Amounts of α,α' -Azobisisobutyronitrile AIBN

No.	AIBN (mole %)	$10^{-3}M_w$ (g/mole)	Polymer		
			$[\eta]$ (ml/g)	T_g (°C)	T_m (°C)
I	0.15	3000	147.6	140	325
II	0.30	1900	108.1	140	327
III	1.5	550	50.65	140	326
IV	3.0	210	30.05	140	327

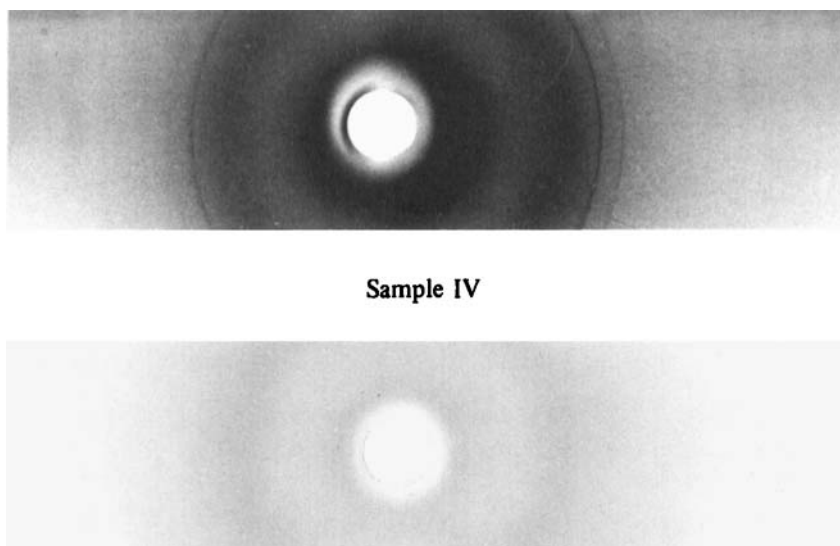


Fig. 2. Debye-Scherrer diagrams of Samples II and IV.

syndiotactic, heterotactic, and isotactic triads [4]. The mole fractions of the triads were determined using a DuPont Curve Resolver giving $X_{SS} = 0.34$, $X_{is} = 0.46$, and $X_{ii} = 0.20$. The mole fractions of the diads as calculated from the β protons decoupled from the α protons were $X_s = 0.57$ and $X_i = 0.43$. The diad fractions calculated from triad fractions using $X_i = X_{ii} + 0.5X_{is}$ and $X_s = X_{ss} + 0.5X_{is}$, respectively, were found to be exactly the same ($X_s = 0.57$, $X_i = 0.43$). The sample is thus of low stereoregularity. Consequently, the number-average sequence lengths [5, 6] of isotactic diads $(L_i)_n = 2 X_i/X_{is} = X_i/(X_s - X_{ss}) = 1.9$ and syndiotactic diads $(L_s)_n = 2 X_s/X_{is} = 2.4$.

The crystallinity observed is very probably due to the presence of small fractions of long stereoregular sequences which can in principle be calculated from the sequence length distribution curve if the diad and triad fractions and the mechanism of stereocontrol are known. Inspection of the diad and triad fractions showed the mechanism to be nearly but not exactly Bernoullian. A correlation between sequence lengths sufficient to induce crystallization requires more complete knowledge of the mechanism of stereocontrol in free radical initiated polymerization of vinyl *t*-p-butylbenzoate.

REFERENCES

- [1] D. A. Lutz and L. P. Witnauer, *J. Polym. Sci., Part B*, **2**, 31 (1964).
- [2] M. A. Osman, Ph.D. Thesis 4203, Swiss Federal Institute of Technology at Zurich, 1968.
- [3] P. L. Magagnini, *Chim. Ind. (Milan)*, **49**, 1041 (1967).
- [4] K. C. Ramey and N. D. Field, *J. Polym. Sci., Part B*, **3**, 63 (1965);
K. C. Ramey and D. C. Lini, *J. Polym. Sci., Part B*, **5**, 39 (1967).
- [5] F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).
- [6] U. Johnsen, *Kolloid-Z.*, **178**, 161 (1961).

Maged A. Osman
Hans-Georg Elias*

*Department of Industrial and Engineering Chemistry
Swiss Federal Institute of Technology at Zurich
Zurich, Switzerland*

Accepted by editor October 9, 1970

Received for publication October 12, 1970

*To whom inquiries should be sent.