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"Modification V" of Poly 4-methylpentene-1 from Cyclopentane Solutions and Gels

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Abstract

A new crystalline structure of poly 4-methylpentene-1 (P4MP1), modification named modification V, is obtained from cyclopentane solutions and gels, for polymer volume fractions between 0.01 and 0.10. The effect of the thermal history imparted to the solution is analyzed. The relation between gelation, polymorphism and existence of helical conformations of P4MP1 in solution is discussed. Modification V is tentatively indexed on the basis of an hexagonal unit cell with dimensions a = 22.17 ± 0.14 Å and c = 6.69 ± 0.02 Å. The crystal transforms into modification I at 130 ± 5°C, the heat of transition being + 15 ± 2 $J.g^{-1}$.

Introduction

Polymorphism, especially prevalent in the higher isotactic polyolefins $(-CH_2CHR-)n$ has been extensively studied for polybutene-1 and polypentene-1. Swelling of poly 4-methylpentene-1 (P4MP1) in volatile solvents, such as cyclopentane and cyclohexane is extensive, despite the high cristallinity of the samples, and induces a structural change in the polymer. A new crystalline pattern, corresponding to modification IV has been observed on the swollen polymer and after evaporation of the solvent (AHARONI et al. 1981)[1]. Modification II crystallizes in xylenes (TANDA et al. 1966a, 1966b) and in decalin (NAKAJIMA et al. 1969) and the high density form III, is formed from the melt under high pressure (HASEGAWA et al.1970). The purpose of this work is to give X-ray and thermal analysis of a new P4MP1 structure, form V, recovered from cyclopentane solutions and gels. These measurements are considered as an indirect information on the P4MP1 conformation in solution.

EXPERIMENTAL

Materials: Cyclopentane (95% pure) was purchased from Chemical Samples Co. (Colombus, OH., USA) and used without further purification. P4MP1 is the same unfractionated sample as in previous work (AHARONI et al 1981).

Sample preparation: The cyclopentane solutions of P4MP1 were prepared in sealed glass tubes. The concentration range was $0.01 \leq \phi_2 \leq 0.10$. Dissolution was achieved by heating the sealed tubes at 85° or 135°C during at least 48 hours. Two cooling rates were then applied; rapid cooling was achieved by quenching the tube at room temperature in the air; slow cooling consisted of a step by step decrease of the temperature of a regulated air oven, at an average maximum rate of 15°C/hour, chosen because it allows to perform a complete cooling cycle in one day. Depending on concentration, maximum heating temperature, and cooling rate, the P4MP1/cyclopentane mixtures appear either as true solutions or clear homogeneous gels. The polymer was then recovered by a slow evaporation of the solvent at room temperature and atmospheric pressure.

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Preparation of oriented samples of modification V: Single crystals of P4MP1 type V could not be grown by cooling a dilute cyclopentane solution at room temperature, because the polymer remains partially soluble at 25°C. Furthermore, a modification V fibre could not be prepared by the usual procedure, since stretching of an unoriented form V sample leads to a form I fibre. However, a partially oriented sample (figure 4) was obtained by swelling a modification I fibre (10:1 stretching ratio) in saturated cyclopentane vapor at 50°C during a few minutes and subsequent drying under vacuum. A similar treatment in liquid cyclopentane did not give satisfactory results due to partial dissolution of the polymer.

APPARATUS

X-ray analysis. Powder patterns for crystalline structure identification were obtained at room temperature, using a flat plate camera, either at atmospheric pressure (ENRAF-NONIUS Diffractis 601, Cu K_α, 40 kV, 20 mA, exposure time 30-90 minutes) or under vacuum (PHILLIPS, P.W. 1730, Cu K_α 35 mA, exposure time 30-60 minutes). X-ray measurements as a function of temperature were performed with a GUINIER-LENNE camera (ENRAF-NONIUS, Cu K_α, 40 kV, 20 mA) operating in parafocus geometry and equipped with linear temperature and film displacement programms. X-ray patterns of Figure 1 have been recorded from films on a microdensitometer (BLAKE INDUSTRIES, Type KD530).

Calorimetry. Temperature and heat of transition were measured on a differential scanning calorimeter (PERKIN-ELMER, DSC-2C, heating rate 10°C/min.)

RESULTS AND DISCUSSION

In gel-forming systems, it can be assumed that the same parameters (thermal history and concentration) which are known to have an influence on the domain of existence and on the properties of gels will have in turn a potential effect on the final crystalline structure of the polymer. A typical example is found in isotatic polystyrene/decalin systems (GIROLAMO et al. 1976, ATKINS et al. 1980) where the occurence of either a gel precursor of an extended polymer chain or a precipitate having the usual conformation depends on the cooling rate . The existence of P4MP1 gels and solutions in non polar solvents over a large temperature interval (DONG 1980) permits the appearance of a variety of conformations in solution and consequently of new crystalline structures. Along the lines of previous work on P4MP1 solutions and gels, the effects of the concentration, the maximum temperature to which the solution have been heated, T_{max}, and the cooling rate are investigated in the present paper. For solutions of P4MP1 in high-boiling solvents like decalin, the intrinsic viscosity-molecular weight relationship at 135°C is characteristic of a random coil conformation (TANI et al. 1973). This temperature was thus chosen as the upper maximum temperature in cyclopentane. The other maximum temperature, 85°C, is the lower limit to ascertain dissolution of the more concentrated cyclopentane solutions.

Table 1 gives the results for cyclopentane solutions of polymer volume fractions between 0.01 and 0.10. P4MP1 recovered from solutions heated at 85°C has a new crystalline structure, designated as modification V. A typical X-ray pattern is given in figure 1 where the diagrams of modifications I, II and IV are also reported for comparison. No effect of the cooling rate is observed and form V is obtained either from solutions ($\phi_2<0.05$) or from gels ($\phi_2\geqslant0.05$). Faster evaporation of the solvent under vacuum or precipitation in a non-solvent diminish the crystallinity of the polymer but do not change its structure. In the course of ongoing work on gels, some slowly cooled concentrated solutions ($\phi_2\leqslant0.50$) have been analysed from which modification V was still obtained.

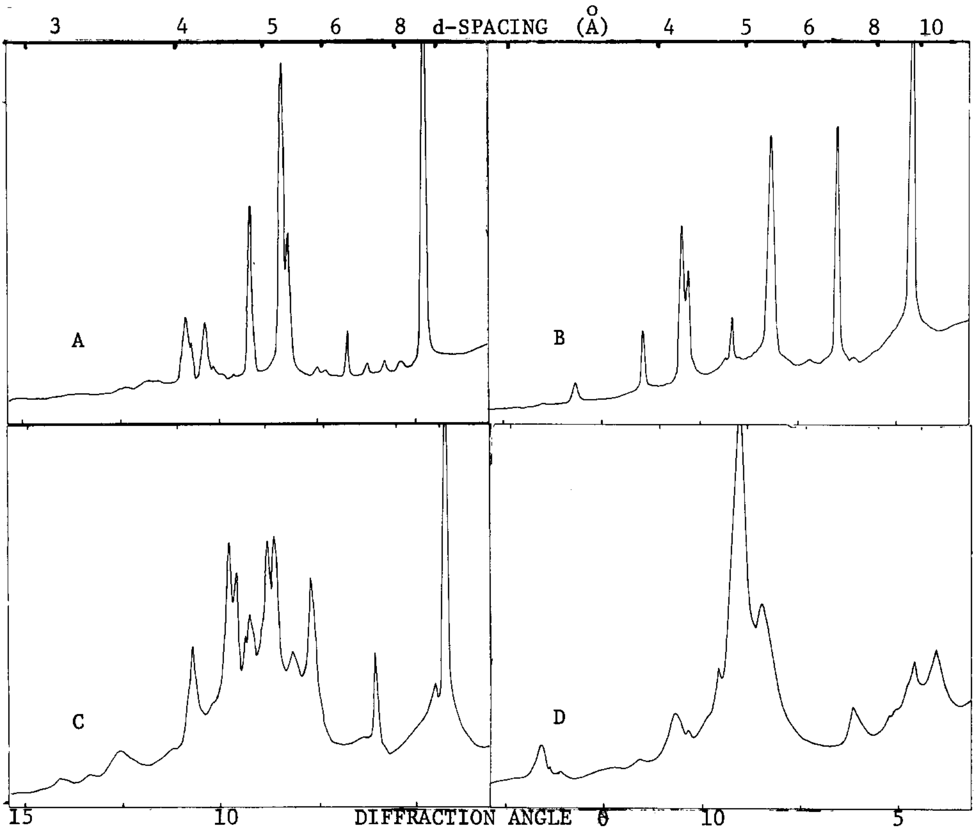

Figure I: Powder X-ray patterns of the different P4MP1 modifications. A: modification I from the melt (KUSANAGI et al. 1978), B: modification II prepared from xylenes (TANDA et al. 1966a, 1966b), decalin (NAKAJIMA et al. 1969) or cyclohexane (REVOL et al. 1981) solutions and gels; C: modification IV recovered from concentrated gels in cyclohexane or after swelling in cyclopentane or cyclohexane at room temperature (AHARONI et al. 1981); D: modification V obtained from cyclopentane solutions and gels (this work).

TABLE I: Crystalline modifications of P4MP1 recovered after dissolution in cyclopentane at polymer volume fractions ϕ_2 between 0.01 and 0.10.

Maximum TEMPERATURE ^{a} T_{max} (^oC)		85^o		135^o	
COOLING RATE ^{b}		S	R	S	R
STATE OF THE SYSTEM^c	$\phi_2 < 0.05$	SOL	SOL	SOL	SOL
	$\phi_2 \geqslant 0.05$	GEL	GEL	SOL	SOL
CRYSTALLINE STRUCTURE^d		V	V	IV+V	II+(VI)^e

a/ Maximum temp. to which the solution has been heated. b/ Cooling rate of the solution from T_{max} to room temp. S: Slow cooling (max. rate 15^{o}C/hour) R: rapid cooling by quenching in the air. c/ After a few hours at room temp. , the solution remained fluid (SOL) or a gel formed (GEL). d/ Crystalline structure of the polymer after solvent evaporation. e/ present in small quantity.

When dissolution is achieved at 135°C, mixed polymer structures were found after evaporation of the solvent, as shown in Table 1. The structure when the solution is quenched from 135° to 25°C, is modification II, already prepared from pentane, cyclo hexane, decalin and xylenes (REVOL et al. 1981). However, the appearance of an extra peak at a spacing $d = 8.5$ Å is indicative of the presence of another structure, provisionally designated for convenience as VI . The intensity of this peak varies from one sample to another, but remains consistently small. The exact nature of this component is not known at the present time, but its presence was already noted in the polymer prepared from cyclooctane solutions (REVOL et al. 1981). Slow cooling of the solutions gave mixtures where the modifications IV and V are the major components. In this case, however, reproducibility was difficult to achieve. Another feature of the high T_{max} systems is the absence of gelation at slow or rapid cooling for $\phi_2 > 0.05$ (Table 1) which, associated with the differences in polymer structures, raises the question of the relation between gelation and polymorphism. A direct relation is excluded, as shown by the following experimental observations: (1) The dilute solutions heated at 135°C do not give modification V (see Table 1) although they are in the same fluid state than the solutions heated at 85°C; (2) Modifications II and IV prepared here from solutions have been also recovered from gels (REVOL et al. 1981, AHARONI et al. 1981). Nevertheless, gelation and polymorphism are likely to have the same origin, namely the helical state of the polymer chain in solution. For P4MP1 solutions, circumstanstial evidence rather than absolute proof of the presence of helices has been given by viscosity and calorimetric data (AHARONI et al. 1981). On the other hand, extensive work by PINO and his group (see review by PINO and NEUENSCHWANDER 1975) on polymers chemically similar to P4MP1, but optically active, such as poly(S)3-methylpentene-1, poly(S)4-methylhexene-1 or poly(S)5-methylheptene-1, leaves little doubt about the existence, in solutions of the most stereoregular polyolefins, of helical main chain sections spiralized in both screw senses. Some information about optically inactive polyolefins was sought by synthetizing copolymers of chiral and non-chiral units; the order in solution is such that the helical conformation of the non-chiral monomeric units is largely present and contributes remarkably to the optical rotation: more precisely, the molar optical rotations of 4-methyl-1-pentene monomeric units included in the left-handed helix of a copolymer with (S)4-methyl-1-hexene or included in the right-handed helix of a copolymer with (R)4-phenyl-1-hexene have been found of the same absolute value (CARLINI et al. 1974). Judging by the large temperature coefficient of the optical rotation, the equilibrium between the different helical conformations, and between the helices and the random coil must be very sensitive to the thermal history of the solution. In line with the above model of the P4MP1 solutions, the lack of gelation after heating the cyclopentane solutions at 135°C may be due to an helix-coil transition, quasi-irreversible in the time of observation. For the moment, it is not possible to know which path the system takes to crystallise in forms IV or V rather than in the more stable form I. This could be either from solutions too poor in helical conformations to form a gel but keeping some helical parts precursor of forms IV-V or directly from the statistical coil.

The existence of order in the polymer melt suggested by the line broadening measurements (WILKES and LEHR 1973) and Brillouin spectroscopy (KRUGER et al. 1980) may have a common molecular origin with that of the gels, i.e., persistence of some helical conformations in non-solid phases.

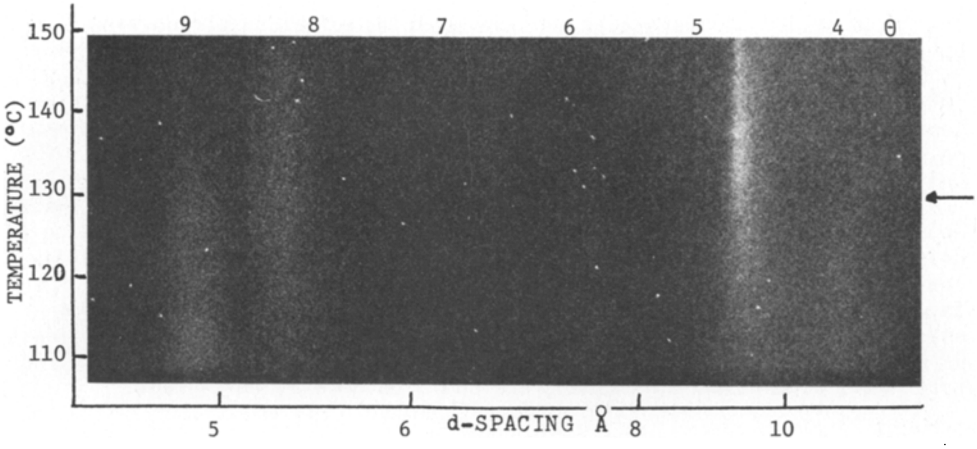

FIGURE 2: X-ray pattern photograph of a modification V sample recorded between 105 and 153°C, using the Guinier-Lenné camera. The V-I transition is observed at 130 ± 5°C (⟶).

CHARACTERIZATION OF MODIFICATION V

Solid-solid transition

Figure 2 gives the X-ray powder pattern of a modification V sample, recorded as a function of temperature between 105 and 153°C, using the Guinier-Lenné camera. The heating rate was 2°C/hour and the film displacement speed behind a 1 millimeter slit was 0.5 millimeter/hour(overall exposure time 24 hours). Despite the diffuse character of the diffraction peaks (also observed on the pattern D of figure 1) due to the constantly low crystallinity of the form V samples, the following changes in the diffraction pattern are observed at 130 ± 5°C:(1) The diffraction bands of modification V at d = 11.0 Å ($\Theta = 4.7^\circ$), d = 9.6 Å ($\Theta = 9.1^\circ$) disappear; (2) an intense band, characteristic of modification I (see figure 1A), appears at d = 9.3 Å ($\Theta = 4.7^\circ$). It is therefore concluded that modification V transforms into modification I at 130 ± 5°C. A broad band at d = 5.3 Å persists in the complete temperature range of figure 2: Due to the broadening of the bands, the expected change from 5.3Å to the 5.3-5.4Å doublet, respectively, characteristic of modifications V and I, cannot be seen.

Figure 3 gives the differential scanning calorimeter thermogram of a modification V sample, heated at 10°C/minute between 60 and 255°C. Beside the usual melting endotherm (onset: 234°C; maximum 240°C; $\Delta H_f = 40 \pm$ J.g^{-1}), a smaller endotherm appears, whose onset and maximum temperatures are respectively 117 and 140°C, quite consistent with the Guinier-Lenné result. The heat evolved during the transition is 15 ± 2 J.g^{-1}.

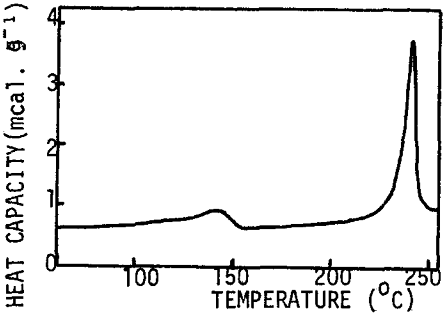

FIGURE 3: DSC trace of modification V sample (heating rate 10°C/mn). Two endotherms are observed: the solid-solid V-I transition around 140°C(ΔH_{tr} : 15 ± 2 Jg^{-1}) and melting around 240°C (ΔH_f: 40 ± 1 Jg^{-1})

The solid-solid V-I transition is irreversible, a feature already found on other P4MP1 solid-solid transitions[2]: for instance, the II-I transition at 75°C (TANDA et al. 1963, REVOL et al. 1981) and the IV-I transition at 90°C (AHARONI et al. 1981). However, modification V is stable for months at room temperature, indicating that it is of metastable rather than unstable nature.

Unit cells parameters

Figure 4 shows the fibre pattern of P4MP1 modification V. The equatorial d-spacings are consistent with the hk0 reflections of an hexagonal unit cell. In the limit of the experimental conditions, no 001 reflexions are observed. However, the entire pattern has been tentatively indexed[3] on the basis of an hexagonal unit cell with dimensions a = 22.17 ± 0.14 Å and c = 6.69±0.02 Å . Table 2 gives the observed and calculated d-spacings as well as observed intensities. Due to the small number of reflections, no hypothesis concerning the space group could be made at this stage.

Table 2: d-spacings and observed intensities of P4MP1 modification V fibre pattern.

d_{obs}^a (Å)	d_{calc}^a (Å)	hkl	I_{obs}^b
11.12	11.09	110	s
9.60	9.60	200	m
7.30	7.26	210	s
5.33	5.33	310	s
4.94	4.92	211	vs
4.63	4.63	301	m
4.20	4.19	410	mw
4.19	4.17	311	m
3.87	3.90	401	vw
3.67	3.63	420	vw
3.57	3.55	411	w
3.20	3.20	600	w
3.17	3.16	202	s
3.06	3.07	511	w
3.00	3.04	212	mw
2.11	2.11	303	vw

The consistent finding that a variety of crystalline structures of P4MP1 are prepared in solvents very similar chemically but of different volatility, indicates that the free volume of the solvent plays a major role in the polymer conformation and contributes as well as the thermal history to determine the final polymer structure. Further studies (CHARLET 1982) including calorimetry, mechanical properties and X-ray measurements of P4MP1 gels in different solvents will give more informations on the conformational equilibria in solution and on the gelation mechanism.

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Added notes

(1) In a previous paper (AHARONI et al. 1981) this modification was designated as form II. Chronological order of discoveries requires reindexation as form IV.

(2) The X-ray pattern of a form I sample, studied by KARASZ et al. (1967),

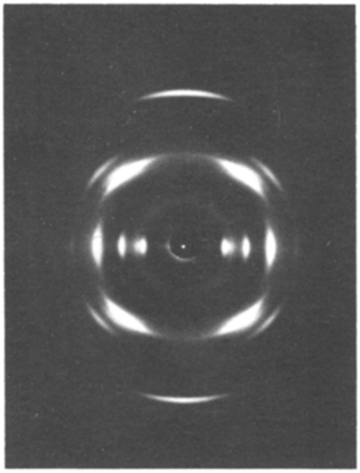

FIGURE 4: Fibre X-ray diagram of modification V. The fibre was vertical and perpendicular to the X-ray beam. The corresponding d-spacings are listed in Table 2.

shows two extra peaks at d = 10.5-11.0 Å and d = 7.4 Å, suggesting the presence of traces of either modification IV or V. However, an endotherm, indicating the irreversible transition from this component to modification I, is observed on the C_p thermogram of the same sample at a temperature as high as $175^{\circ}C$, precluding a definite conclusion about the nature of this polymorphic impurity.

(3) Unit cell dimensions have been evaluated by a least square fit method on linearized data using ($(d_{hkl})^{-2}(h^2+k^2+hk)^{-1}$) and ($l^2(h^2+k^2+hk)^{-1}$) as variables.

References

AHARONI, A., CHARLET, G., and DELMAS, G., Macromolecules, 14, 0000 (1981)

ATKINS, E.D.T., ISAAC, D.H. and KELLER, A., J. Polym. Sci., Phys., Ed, 18, 71 (1980)

CARLINI, E., CIARDELLI, F., LARDICCI, L. and MENICAGLI, R., Makromol Chem. 174, 27 (1974)

CHARLET, G.Ph.D.Thesis McGill University, Montreal, Canada, 1982

GIROLAMO, M., KELLER, A., MIYASAKA, K. and OVERBERGH, N., J. Polym. Sci., Phys, Ed, 14, 39 (1976)

HASEGAWA, R., TANABE, Y., KOBAYASHI, M., TADOKORO, H., SAWAOKA, A. and KAWAI, N., J. Polym. Sci., A2, 8, 1073 (1970)

KARASZ, F.E., BAIR, H.E. and O'REILLY, J.M., Polymer, 8 (10), 547 (1967)

KRUGER, J.K., PEETZ, L., WILDNER, W. and PIETRALLA, M., Polymer, 21, 620 (1980)

KUSANAGI, H., TAKASE, M., CHATANI, Y. and TADOKORO, H., J. Polym. Sci., Polym. Phys. Ed., 16, 131 (1978)

NAKAJIMA, A., HAYASHI, S., TAKA, T. and UTSUMI, N., Kolloid Z.Z. Polym., 234, 1097 (1969)

PINO, P. and NEUENSCHWANDER, P., J. Polym. Sci. Symposia, 171 (1975)

REVOL, J.F., CHARLET, G. and DELMAS, G., submitted for publication

TANDA, Y., Y. IMADA, K. and TAKAYANAGI, M., Kogyo Kagaku Zasshi, 69, 1971 (1966a)

TANDA, Y., KAWASAKI, N., IMADA, K. and TAKAYANAGI, M., Report Progress Polymer Physics Japan, 9, 165, (1966b)

TANI, S., HAMADA, F. and NAKAJIMA, A., Polymer J., 5, (1) 86 (1973)

WILKES, C.E. and LEHR, M.H., J. Macromol. Sci. Phys., B7, 2, 225 (1973)

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