is aligned precisely in the radial direction although no such requirement is set by symmetry rules applicable to monoclinic crystals; and (d) over a limited range of crystallization temperature, poly(ethylene sebacate) solidifies in a hitherto unknown polymorphic form. Properties of this polymorph are to be described in part 2.

Acknowledgment. It is a pleasure to acknowledge assistance from several colleagues. Thanks are due to W. P. Slichter for a sample of polymer, to D. J. Freed and A. M. Mujsce for synthesis of a sample of relatively high molecular weight, to M. Y. Hellman for characterization of molecular weight, and to F. J. Padden, Jr., and A. J. Lovinger for helpful criticism of the manuscript.

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Optical Behavior and Polymorphism in Poly(ethylene sebacate). 2. Properties of the New Polymorph

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ABSTRACT: The newly recognized polymorph of poly(ethylene sebacate) is shown to be metastable and to undergo transformation to the stable monoclinic form at temperatures in the range 70–74.5 °C. The transformation is extremely slow at the lower limit of this range and virtually instantaneous at the upper limit; it appears to occur in the solid state. It is shown that nucleation of the polymorph is suppressed by the presence of moisture absorbed in the polymer, by contact of "dry" polymer with water at crystallization temperature, or by the presence of sebacic acid often remaining as a contaminant after synthesis. These phenomena appear to be related to a more congested packing of polar groups than is found in the known monoclinic form. Carbonyl groups of one molecule are deeply interdigitated with ester linkages of the next, providing an energetically propitious head-to-tail arrangement of aligned dipoles but leaving no room for favorable interaction with other dipoles of foreign origin. A likely crystal structure is proposed in which the dipole alignment just referred to seems certain but many important details still remain to be resolved definitively.

In a companion paper[1] (part 1), evidence has been presented for the existence of a new polymorphic form of poly(ethylene sebacate). We shall now describe the properties of this polymorph and, in particular, its metastability and transformation to the known monoclinic form, the sensitivity of its nucleation to the presence of polar contaminants (notably moisture), and its likely crystal structure.

Metastability and Transformation to the Stable Form

Distinctive differences between X-ray diffraction patterns of the two polymorphic forms of poly(ethylene sebacate) have already been noted in part 1. These are seen again in the diffractometer traces shown in Figure 1, which illustrates very clearly the relative displacement and marked difference in intensity of 020 reflections from the two crystal forms. Traces such as these provide a convenient and rapid means of assessing the relative amounts of the two forms present in a given sample. By this means, we find that the new polymorph is stable indefinitely at room temperature and remains unchanged if maintained at its crystallization temperature (56 °C in most of our experiments—see part 1 for fuller details) for at least 20 h after solidification. If the polymorph is heated at 1 °C/min to various higher temperatures and then examined by X-ray diffraction at room temperature, we find that the first sign of transformation occurs at 70 °C in the form of a slight shoulder on the 020 peak similar to, but much less pronounced than, that shown in Figure 1c. This new reflection continues to grow very slowly in intensity with further heating at 70 °C over a period of several hours. In specimens heated to 73 °C, transformation to the stable form is essentially complete after 5-min residence at this temperature. In specimens heated to 74 °C and examined immediately, however, there is still a discernible 020 peak due to the new polymorph but, when specimens are maintained at this temperature, it disappears very rapidly and leaves a trace corresponding to the pure stable form. If specimens are heated at 1 °C/min under the polarizing microscopy, there is an abrupt increase in birefringence of type II spherulites (of the new polymorphic form) in passing through 74.5 °C, indicating that at this temperature the transformation is essentially instantaneous. The transformed spherulites then melt at the same temperature as type I or type II spherulites (of the stable form).

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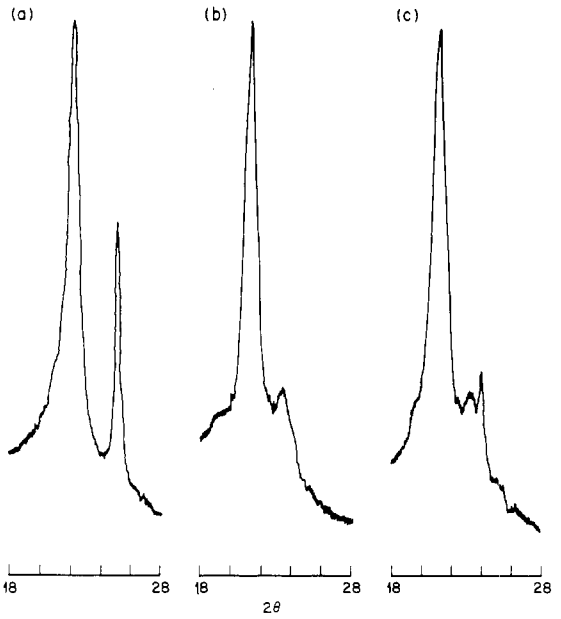

Figure 1. X-ray diffractometer traces in the region $18° \leq 2\theta \leq 28°$ of (a) stable polymorph (monoclinic), (b) metastable polymorph, and (c) a sample containing a small amount of stable polymorph in a matrix of metastable polymorph.

These various observations establish the new polymorph as a *metastable* crystal form. Whether transformation to the stable form occurs in the solid state or involves melting and recrystallization, however, is less certain. In favor of the first possibility we may cite the preservation of spherulitic morphology with so little change during transformation (see part 1). Again, if we crystallize samples at 56 °C, heat them at 1 °C/min to 74 °C and then, on the one hand, quench some of them immediately in ice water and, on the other, transfer some of them immediately to a hot plate at 56 °C, we find subsequently that they all give identical X-ray diffractometer traces showing the presence of an overwhelming preponderance of the stable form. Molten polymer would crystallize in different forms in the two cases (again see part 1) and, as we shall show later, the crystal growth rate of the stable form at 74 °C is extremely slow ($<2 \times 10^{-3}$ μm/s) so that appreciable solidification of such a melt at 74 °C before cooling is unlikely. The point is not unambiguous, however, and is clouded further by the observation that with rapid heating (10 °C/min) spherulites of the metastable form (type II) do melt at a temperature close to 74.5 °C. At this heating rate, the stable form melts at 76 °C while at 2 and 1 °C/min it melts at 77.3 and 78.5 °C, respectively. A complicating factor, apparently, is the dependence of melting characteristics upon crystal thickness, which probably increases at a finite rate with increasing temperature in the manner commonly encountered in lamellar polymer crystals.

Differential scanning calorimetry also supports the view that transformation occurs in the solid state but, again, not definitively. In comparing thermograms of samples crystallized at 56 and 63 °C (i.e., in different polymorphic forms) and heated at the same slow rate (see Figure 2), we find that there is a point of inflection at 70 °C in the case of the metastable polymorph. This could be interpreted as the beginning of a small exothermic peak superimposed upon, but almost engulfed by, a much larger endothermic peak with a maximum at approximately 73 °C. If correct, this means that the difference in enthalpy between the two polymorphs is a very small proportion (3% perhaps) of the enthalpy of fusion. It is evident, however, that a variety

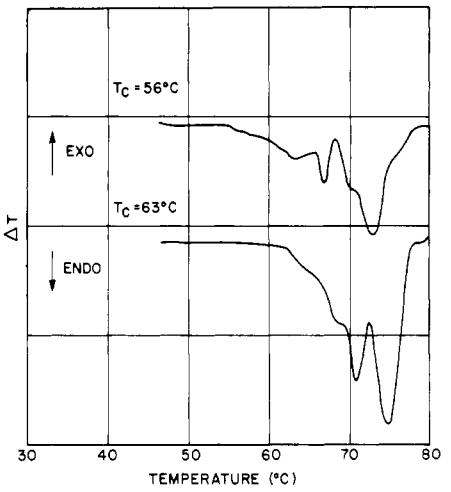

Figure 2. Thermograms of metastable (upper curve) and stable (lower curve) polymorphs heated at 1 °C/min. Note the point of inflection in the upper curve at 70 °C. Sample sizes are different in the two cases.

of endothermic processes occur above the crystallization temperature and the interpretation just suggested, though reasonable, is not unequivocal. The smaller endothermic peak at 67 °C is certainly *not* associated with transformation between forms, a point that has been checked by additional X-ray studies. However, it is significant that as heating rates are varied and the positions of endothermic peaks change, there is always some indication of the onset at about 70 °C of a slight exothermic component in thermograms of the metastable polymorph. Our view is that the weight of evidence strongly suggests that the transformation from metastable to stable polymorph takes place in the solid state.

Conditions Influencing Nucleation of the Metastable Polymorph

An unusual feature of the metastable polymorph was discovered fortuitously by plunging open films of molten polymer on Kapton polyimide sheet into a water bath at 56 °C to achieve more rapid equilibration of temperature than is attainable by transferring to a hot plate at that temperature. Such films then gave X-ray diffractometer traces corresponding to pure stable polymorph whereas polymer crystallized dry at the same temperature was known to crystallize exclusively in the metastable form. However, removing the films from their Kapton substrates and turning them over so as to expose their dry interfaces to the X-ray beam, which in this experiment samples a thin surface layer only, we obtained traces of the pure metastable form. Contact with water apparently caused nucleation of the stable form, which then grew inward as a transcrystalline layer until it encountered spherulites of the metastable form nucleated in the usual manner in the interior of the dry polymer. Rapidity of cooling is not a factor since molten films plunged into silicone oil at 56 °C crystallized exclusively in the metastable form. Neither is lack of stability of the metastable polymorph (once formed) in the presence of water since films crystallized dry at 56 °C could subsequently be immersed in water at 56 °C for many hours without perceptible signs of transformation to the stable form.

The effects just described are completely reproducible and the role of water is further exemplified by equilibrating the polymer with saturated water vapor at room temperature prior to fusion and crystallization. If a film of melt is then maintained at 150 °C for 10 min before crystallization at 56 °C, only the metastable polymorph is formed.

On the other hand, films of "wet" polymer that are just melted momentarily at 85 °C and then crystallized at 56 °C consist almost exclusively of the stable polymorph. Fusion for longer times or at higher temperatures, followed by crystallization at 56 °C, produces mixtures of the two forms intermediate between these extremes; however, relative abundances of the two polymorphs are not very reproducible, as is scarcely surprising in view of the poorly controlled expulsion of moisture. Polymer crystallized in the stable polymorphic form at 56 °C, either in "wet" polymer or in dry films nucleated in contact with water, forms negative spherulites similar to those previously designated type I in part 1.

Moisture uptake by poly(ethylene sebacate) is typical of most polyesters. Thoroughly dried samples crystallized in the stable form, when equilibrated with saturated water vapor at room temperature, take up about 0.75% by weight of water, and similar samples crystallized in the metastable form take up about 0.6%. The difference may merely reflect a difference in crystallinity, but, in any event, these concentrations are much less than that required (7.6%) to form a stoichiometric hydrate involving one water molecule per chain repeat.

Water is not unique in its influence on nucleation of the stable polymorph at temperatures at which pure dry polymer crystallizes in the metastable form. It had earlier been noted that before purification by dissolution and reprecipitation (see part 1), the polymer always included some spherulites of the stable form regardless of crystallization temperature. (Figure 1c is, in fact, a diffractometer trace of such a sample crystallized at 56 °C—to be compared with Figure 1b, the corresponding trace for purified polymer.) It was suspected that this was attributable to traces of sebacic acid formed by hydrolysis of unreacted sebacoyl chloride remaining from the synthesis. This interpretation was confirmed by lightly dusting sebacic acid onto a film of poly(ethylene sebacate) before fusion (above the melting point of the acid) and crystallization at 56 °C. The crystallized film then gave a diffractometer trace corresponding to the stable form without appreciable signs of metastable polymorph being present in the surface layer. The 004 reflection of sebacic acid lies close to the 020 reflection of the stable form of the polymer but is, nevertheless, strong enough and sufficiently separated in Bragg angle for it to be certain that the sebacic acid was not contributing its own pattern and confusing the data. No attempt has been made to determine exactly how much sebacic acid is required to change nucleation characteristics of the polymer but it appears to be of order 5% or less. Polar interactions clearly play an important role in determining which crystal form is nucleated.

Relative Crystallization Rates of the Two Polymorphs

In Figure 3, radial growth rates of ringed spherulites of the stable polymorph (type III) measured over the range 59–65 °C in crystallization temperature are compared with that of spherulites of the metastable polymorph (type II) grown at 57 °C. Since the latter spherulites nucleate densely and grow rapidly, the experimental error is considerable. Nevertheless, it is evident that crystals in the metastable form grown radially at about twice the rate of those of the stable form at roughly comparable temperatures.

In order to assess growth rates of the stable form at 74 °C, the temperature at which transformation between forms occurs rapidly, spherulites of type III were grown to convenient size at 63 °C and then heated to the higher temperature to observe continuing growth into the surrounding melt. Further growth was extremely slow, $\leq 2 \times 10^{-3}$ μm/s.

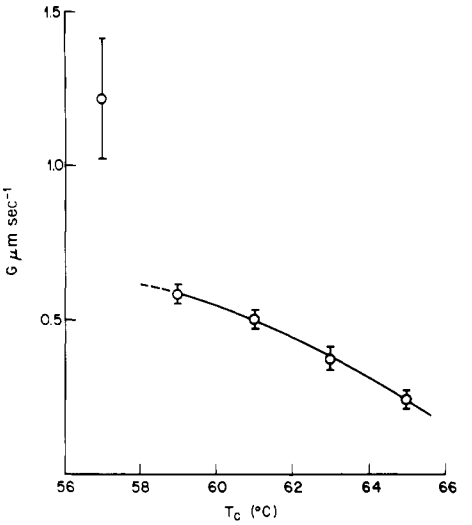

Figure 3. Radial growth rates of spherulites of the stable polymorph grown in the range 59–65 °C and of spherulites of the metastable polymorph grown at 57 °C.

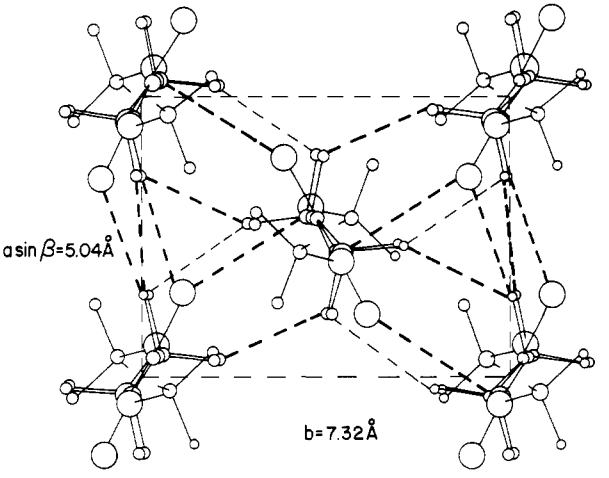

Figure 4. Chain-axis projection of monoclinic poly(ethylene suberate), after Turner-Jones and Bunn.[2] Except for addition of a methylene group in the chemical repeat, the chain-axis projection of the stable monoclinic structure of poly(ethylene sebacate) is believed to be essentially identical with this, and cell dimensions marked are for this polymer. Contacts determining intermolecular distances are shown by dashed lines, the heavier dashed lines representing particularly tight contacts.

Structural Differences between Stable and Metastable Polymorphs

It has already been suggested in part 1 that the stable polymorph has a structure similar to that previously determined for poly(ethylene suberate).[2] The chain repeat is longer, and small tilts of the chains with respect to the *c* axis may be slightly different owing to the inclusion of additional methylene groups in the acid residue. Relative intensities of X-ray and electron diffraction patterns are consistent with such a view. Figure 4 shows the *c*-axis projection of the poly(ethylene suberate) structure, and we assume that this also gives a reasonably accurate representation of the stable form of poly(ethylene sebacate). Planar zigzag methylene sequences make angles of 40° with respect to the *ac* plane and, on this basis, it is clear how projecting carbonyl oxygen atoms contribute to broadening of 200 reflections and how electrical polarizability along the $a \sin \beta$ direction (α^* axis) is greater than that along the *b* axis.

Recalling the properties of the metastable polymorph as described in part 1, it is clear that as compared with the structure of the stable form, chains must be rotated so as to bring planar zigzag methylene sequences more into parallelism with the β axis. This would (a) cause slight contraction of the $a \sin \beta$ dimension of the unit cell and sharpen the corresponding 200 X-ray reflection, (b) increase the b axis of the unit cell and, through distortions caused by the protruding carbonyl oxygen atoms, cause broadening of the 020 reflection and (c) increase electrical polarizability along the b axis at the expense of that along the orthogonal $a \sin \beta$ direction. The important question, however, is whether or not the chains rotate symmetrically toward the b axis so as to preserve the symmetry of the $P2_1/a$ space group.

Calculation of interatomic distances based upon atomic coordinates given by Turner-Jones and Bunn[2] show that critical contacts between chains are as indicated by the dashed lines in Figure 4. These contacts would obviously present formidable barriers to symmetrical rotation of the chains unless the b axis were appreciably lengthened. This axis is, in fact, 3.8% longer in the metastable polymorph, but this would allow only a slight rotation, quite inadequate to account for the marked weakening of 020 reflections. Based upon different staggering of chains in the c direction, there are two other possible ways of packing chains with the same conformation into the unit cell of the stable polymorph without changing the c-axis projection. One of these, considered but dismissed for valid reasons by Turner-Jones and Bunn in the case of poly(ethylene suberate), has $P2_1/a$ symmetry, the other $P2_1$; however, neither of these offers a more attractive possibility for rotation of chains to form a structure consistent with the properties of the metastable polymorph and with molecules in two orientations that have ac as a glide plane.

A more likely possibility is that chains in the metastable polymorph all have essentially the same orientation with the planes of their zigzags aligned along, or very close to, one diagonal of the c-axis projection. It will be noted in Table I of part 1 that there are three $hk0$ reflections (h, $k \neq 0$) from the metastable polymorph, all of whose spacings are consistent with the chain-axis projection of the unit cell being orthogonal. Preliminary calculations show that such a structure (see Figure 5) would permit molecular packing in a unit cell whose c-axis projection has the measured lateral dimensions, 5.01 and 7.6 Å. Chains lined up along the face diagonal are probably at the same height, or very close to it, since this would not only allow the projecting carbonyl oxygen of one molecule to fit into a cleft in the next molecule between the chain oxygen and the pair of hydrogen atoms on the first carbon atom of the acid residue but would also permit optimal interdigitation of methylene hydrogens. The structure would be strained at carbonyl oxygen contacts, however, O–O and O–H distances being computed as 2.65 and 2.53 Å. The first distance is only 0.15 Å less than commonly found, and the second only 0.02 Å less than an O–H distance in the accepted structure of poly(ethylene suberate); slight rotation of chains as a whole or minor distortions of conformation could easily accommodate this congestion. Distances between interdigitating methylene hydrogens are about 0.2 Å longer than H–H contacts in the suberate, implying fairly loose contacts consistent with a 3% lower density of this polymorph (see part 1). The tight packing at carbonyl oxygen contacts in combination with this looseness of the paraffinic sequences could well account for the diffuseness of 020 reflections. Similarly, the fact that carbonyl oxygen contacts have little direct effect on intermolecular distances in the orthogonal direction would explain sharpening of the 200 reflection and slight contraction of the corresponding spacing. Contact between successive sheets of molecules would be made exclusively between methylene hydrogens which are spaced comfortably at about 2.5 Å apart. As compared with the stable polymorph, the intensification of 200 reflections, weakening of 020 reflections, and closer approach to electrical isotropy transverse to the chain axis would all follow qualitatively.

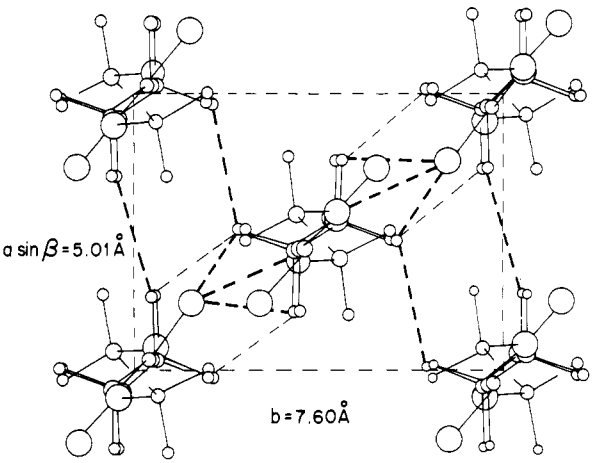

Figure 5. Chain-axis projection of the proposed structure of the metastable polymorph of poly(ethylene sebacate) adapted, with the same qualifications, from Figure 4. Critical contacts are again represented by dashed lines. The essential feature, relative to Figure 4, is the parallelism of all chains in cross section to one diagonal of the projected cell. Finer details are tentative pending further study.

One might wonder why such a structure, both strained and relatively open at the same time, might be formed at all. However, it has one appealing feature in that electrical dipoles associated with carbonyl groups are aligned head-to-tail in an energetically very favorable way. These groups, incidentially, are the sites to which water molecules or other polar groups are attracted, and the fact that they are in much more crowded surroundings in this proposed structure than in the stable polymorph may well underlie the reluctance of "wet" polymer, or polymer contaminated by sebacic acid, to nucleate in the metastable crystal form. The nucleating influence on "dry" polymer of an interface with water is presumably of similar origin. It is not immediately obvious, however, why the metastable polymorph crystallizes appreciably faster than the stable polymorph.

Further work is needed to clarify details of the structure of the metastable polymorph, which has so far proved difficult to prepare in the form of an oriented fiber unadulterated by stable polymorph. If our present views are correct, one can indeed compute many interplanar spacings on the basis of a monoclinic unit cell as we have done earlier in part 1, but an appropriate crystallographic unit cell (nonprimitive) which is easily related to that monoclinic cell would, in fact, be triclinic with approximate dimensions $a = 5.39$ Å, $b = 7.60$ Å, $c = 16.76$ Å, $\alpha = 104.8°$, $\beta = 111.7°$, $\gamma = 72.4°$ ($Z = 2$), and the space group would be $P\bar{1}$. The obliquity of the cell is dictated by displacements in the c direction between molecular sheets so as to preserve essentially the same d_{001} spacing as found in the stable polymorph. Transformation from the metastable to the stable structure would involve both a rotational "flip" of the central chain in each cell and also slight rotational and axial adjustments of the remaining chains. Barriers to the "flip" would be considerable (as is evident

from Figure 5) and its occurrence would presumably involve cooperative motions of many chains.

It is to be emphasized, however, that while the structure we suggest seems the most likely in terms of presently available evidence, there is at least one other possibility. Alignment of chains along, or close to, one diagonal of the c-axis projection seems certain, but a different c-axis stagger along that diagonal is conceivable that would result in a different obliquity of b and c axes. This structure would not allow optimal interdigitation of methylene hydrogens but departure from this condition would be modest but, since the packing of methylene sequences is loose to begin with, this is not a telling argument. In neither case is it clear why the d_{001} spacing is essentially the same in the two crystal forms; this spacing is determined both by chemical repeat distance and by stagger between molecular sheets depending largely upon interactions that do not involve ester linkages in a crucial way and are, therefore, difficult to assess ab initio. When the symmetry of the new polymorph is better characterized, it may prove necessary to revise some of the tentative conclusions in part 1 regarding its optical properties. It will be recalled that the only disagreement of substance in our quantitative analysis of optical behavior arose in connection with this polymorph, though a credible explanation was proposed that did not require a drastic change in viewpoint.

It is suggested that the stable monoclinic form of the polymer should hereafter be designated α-poly(ethylene sebacate) and the metastable polymorph be called β-poly(ethylene sebacate).

Conclusions

Principal conclusions are (a) that the new polymorph of poly(ethylene sebacate) is metastable, (b) that it transforms to the stable monoclinic form at temperatures above 70 °C, apparently within the solid state, (c) that nucleation of this form is suppressed by traces of moisture or sebacic acid (probably other polar contaminants as well), and (d) that its crystal structure differs from that of the stable form principally in that the plane of the central chain in the unit cell lies parallel to those of the corner chains and not at a large angle to them as in the stable monoclinic form. This difference in structure accounts qualitatively for all the known properties of the polymorph, including the sensitivity of nucleation to polar contaminants. A full determination of structure and symmetry, however, requires an X-ray diffraction study of an oriented fiber free of the stable form. Production of such a fiber has not yet been achieved but work is continuing.

Acknowledgment. Assistance from D. W. Dahringer and L. H. Sharpe in obtaining DSC data, and from A. J. Lovinger and F. J. Padden, Jr., in the form of critical reviews of the manuscript, is gratefully acknowledged.

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Two-Dimensional J Spectroscopy: ^{1}H NMR of Polysaccharides. Application to Capsular Heteroglycans and Labeled Cellulose Triacetate

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ABSTRACT: ^{1}H two-dimensional J spectroscopy has been investigated in the case of polysaccharides: capsular heteroglycans and cellulose triacetate. The results show the usefulness of this technique regarding identification of overlapping protons and coupling constant measurements, leading to an easier analysis of ^{1}H spectra. In particular, anomeric configurations of rhamnose-containing polysaccharides were confirmed accurately. Another application of this technique concerned deuterated cellulose triacetate, for which an improved resolution allowed a differentiation of the possible isotopomers on the basis of their isotopic effect.

Although many important studies of proton two-dimensional spectroscopy have already been published,[1-4] none of them has been devoted to polysaccharides or other stereoregular polymers. As a matter of fact, it is well-known that for polysaccharides and polymers, magnetic field inhomogeneity effects, high-viscosity solutions, and short spin–spin relaxation times (T_2) contribute to broaden the lines in normal one-dimensional ^{1}H NMR spectra. With the substantial resolution enhancement obtained by two-dimensional NMR experiments and with the possibility of measuring chemical shifts and coupling constants in a region of the spectrum where many signals overlap (as shown by Hall et al.[3]), problems relevant to polysaccharide NMR should be overcome, particularly in the case of complex polysaccharides such as capsular polysaccharides of *Klebsiella* (containing more than one residue in the repeating unit) and labeled polysaccharides containing several isotopomers, i.e., a mixture of multiply labeled compounds.

Experimental Methods

Samples. The undeuterated or deuterated cellulose triacetate was obtained by acetylation of biosynthesized cellulose by *Acetobacter xylinum* from glycerol or *sn*-[1,1,2,3,3-$^2H_5$]-glycerol as a carbon source.

sn-[1,1,2,3,3-$^2H_5$]-Glycerol was prepared according to Koch and Stuart's method[5] in the presence of Raney nickel catalyst. Deuteration was effected to the extent of 80%. Bacterial cellulose was grown in water according to Hestrin's experimental conditions.[6] The deuterated cellulose was labeled at approximately 46% on each of the six carbon atoms, as determined by one-dimensional proton analysis.[7]

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