

# Comb-Type Polymers and Their Interaction with Wax Crystals in Waxy Hydrocarbon Fluids: Wide-Angle X-Ray Diffraction Studies

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## SYNOPSIS

We report the results of our wide-angle X-ray diffraction (WAXD) studies on the interaction of various comb-type acrylate polymers, synthesized in our laboratories, with waxes crystallizing out below the cloud point of an indigenously available high-wax commercial diesel fuel. These copolymers were made from monomers from  $C_8$  to  $C_{24}$  carbon numbers, which covers the average carbon number, viz.,  $C_{16}$ – $C_{22}$ , of most of the commercial diesel fuels. The influence of the pendant chain on the crystallization process of *n*-alkanes below the cloud point of the fuel has been assessed, for the first time, to the best of our knowledge, by this method. Wax crystals, isolated by this procedure, are basically hexagonal, with some features relating to mal-structures and have similarity to the comb-type polymers with more than eight carbon atoms in their side chains. Effective pour-point depressants showed distinctive changes in the diffraction pattern of the low-angle, i.e., larger than van der Waals (LVDW) peaks, usually a general shift to higher angles, and in some cases, a distinct split. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Comb-type polymers have been extensively used as wax crystal modifiers for improving the cold-flow properties of a large variety of waxy petroleum fluids ranging from middle distillates (diesel fuels) through residual fuels and crude oil,<sup>1–8</sup> which has been the most cost-effective means of upgrading these products. Chichakli,<sup>9,10</sup> for the first time, used X-ray diffraction data to elucidate the mechanism of action of cold flow improver additives in late 1960s. Even as recently as 1991, this work has been cited<sup>11</sup> as a principal reference in this area. Several investigators have subsequently carried out structural studies on wax crystals and comb polymers using different methods including X-ray diffraction with a view to finding a rational explanation for the wax crystal modification by these polymers.<sup>12–16</sup> Plate and Shibaev<sup>13</sup> reviewed the work on the structure of

comb-type polymers. Blumstein et al.<sup>17–20</sup> reported mesomorphic behavior of such polymeric systems.

Molecular organization in these polymers is classified into two main groups: smectic (lamellar or layered structure) and nematic (directional structure). Muller<sup>21</sup> studied the low-angle spacing in X-ray diffraction corresponding to the length of the completely extended side chain of polymers. The higher-angle spacings correspond to the hexagonal form of the polymorphic alkanes. Kaufman et al.<sup>22</sup> found a sharp spacing of 4.2 Å both in long-chain alkyl acrylate polymers and *n*-paraffin crystals, a similarity that was maintained even when the backbone of the acrylate polymer was not stereoregular. According to Jordan and his co-workers,<sup>23,24</sup> up to 8–9 methylene groups in the side chain of a polymer tend to remain in an amorphous state. Methylene groups beyond this number alone were observed to participate in crystallization. Hsieh et al.<sup>25</sup> noted partial intercalation of the side chain in a series of comb-like partially stereoregular polymers including poly(*n*-octadecyl methacrylate). A similar conclusion was arrived at by Ailhaud and his associates<sup>26</sup>

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in the case of highly syndiotactic poly(*n*-octadecyl methacrylate).

All these studies led to the conclusion that the main chain (backbone) and part of the side chain (pendant groups) remain in the amorphous zone (disordered phase) and that only a fraction of the side chain is in the crystalline phase. This is in conformity with the suggestion of Jordan et al.,<sup>23,24</sup> but is in contrast with the views of Plate and his co-workers.<sup>27</sup> The present communication describes our results on the interaction of various comb-type polymers, synthesized in our laboratories, with *n*-alkanes isolated from a well-defined indigenous high-wax commercial diesel fuel using wide-angle X-ray diffraction (WAXD) studies, undertaken with a view to developing effective cold-flow improvers to these fuels.

## EXPERIMENTAL

The synthesis and characterization of a series of alkyl acrylate monomers with the alkyl group ranging from *n*-C<sub>8</sub> to C<sub>30</sub> and their homo- and copolymers have been described.<sup>28,29</sup> Polymerization<sup>25</sup> was carried out under standard free-radical conditions, carrying the conversion to near completion. The reactivity ratios among the long-chain alkyl acrylate monomers have been assumed to be nearly equal. The effect of these comb polymers on the wax crystal habit was examined in an Indian commercial high-speed diesel fuel (summer grade) with a high pour point of 12°C. The total *n*-alkanes (wax L) of the

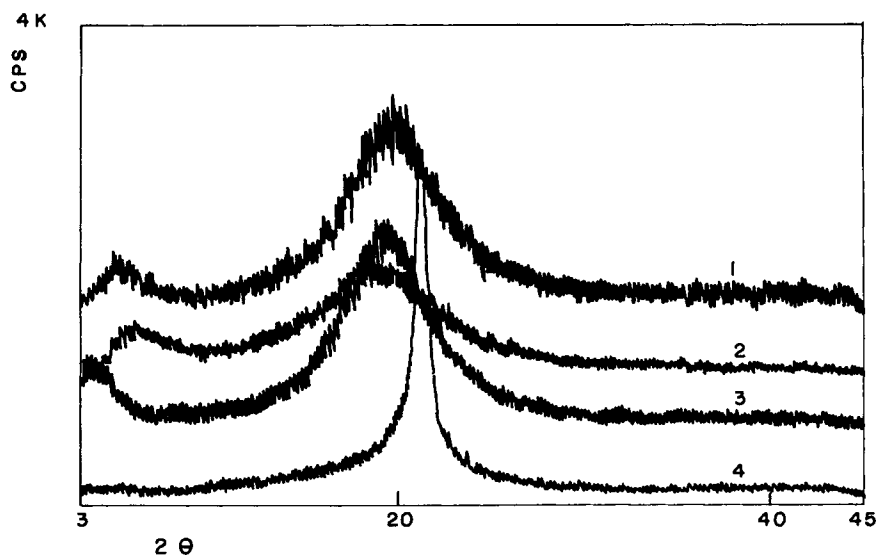
fuel were isolated by addition with urea following the standard procedure. Wax samples were also obtained by cooling the diesel fuel to 12°C without additive (wax K) and to 3°C after treatment with a cold-flow modifier additive X, developed in our laboratories at the 400 ppm level (wax M). The additive X is a poly(alkyl acrylate) copolymer with proper spacing between long side chains and (wax N) was a blend of wax L with 1200 ppm of additive X.

## X-ray Diffractograms

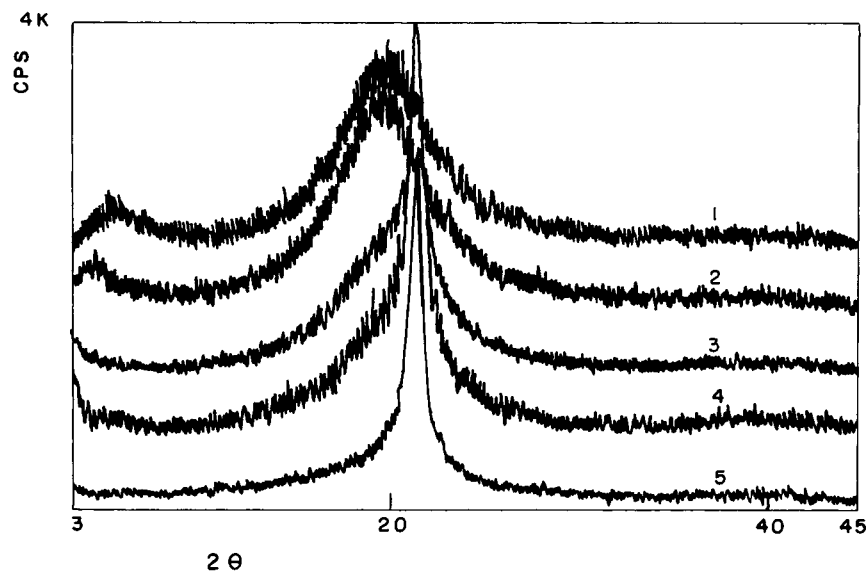
The wide-angle X-ray diffractograms were obtained on a Rigaku Model D/MAX IIIB, with CuK $\alpha$  radiation at 35 kV and 20 mA, in the wide-angle range of  $3^\circ < 2\theta < 45^\circ$ .

## RESULTS AND DISCUSSION

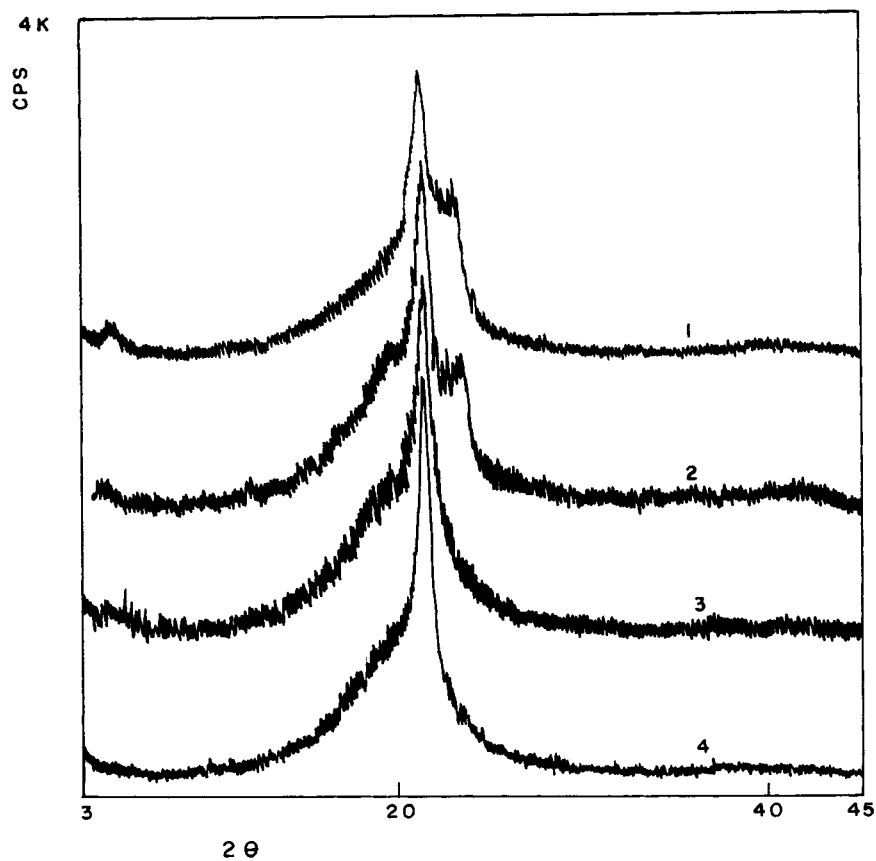
The X-ray diffractograms of comb-type homo- and copolymers used in the present study are shown in Figures 1–3. Their principal characteristics are summarized in Table I. Around 20°, a strong central peak corresponding to a *d* value of 4.1–4.6 Å was given by several long-chain acrylate and methacrylate polymers, which was attributed to the van der Waals (VDW) contact of nonbonded atoms.<sup>30</sup> In addition, one or more peaks appear in the low-angle region (LVDW). Their *d* values are greater than that of VDW packing. Their intensities are moderate to weak. This indicates the presence of structures



**Figure 1** WAX diffractogram series: (1) poly(*n*-octyl acrylate); (2) poly(2-ethylhexyl acrylate); (3) poly(*n*-dodecyl acrylate); (4) poly(*n*-octadecyl acrylate).



**Figure 2** WAX diffractogram series: (1) poly(*n*-octyl acrylate); (2-4) poly(*n*-octyl-*co*-*n*-octadecyl acrylate) samples obtained using monomer mole ratios 3 : 1, 1 : 1, and 1 : 3, respectively; (5) poly(*n*-octadecyl acrylate).



**Figure 3** WAXD patterns of copolymers of *n*-octyl acrylate with (1) *n*-docosanyl-, (2) *n*-tetracosanyl-, (3) *n*-eicosanyl-, and (4) *n*-octadecyl acrylates obtained with 1 : 1 monomer ratios.

**Table I Interplanar Spacings of Some Long-chain Acrylate Homo- and Copolymers**

Polymer	LVDW <sup>a</sup>		VDW <sup>b</sup> (100)			(110) $d_2/d_3 =$		
	$d_1$ (Å)	$2\theta$	$d_2$ (Å)	$2\theta$	Size (nm)	$d_3$ (Å)	$2\theta$	$\sqrt{3}$
Homopolymer								
PA-8	17.4	5.0	4.5	19.5	22.9	2.7	16.5	1.6353
PEHA	14.7	5.9	4.6	19.0	21.5	2.1	38.0	2.1474
PA-12	21.4	4.1	4.5	19.4	28.4	2.2	32.0	2.0312
PA-18	16.6	5.3	4.1	21.4	80.5	2.2	26.3	1.8325
Copolymer								
A8-A18								
1 : 3 (mol %)			4.1	21.4	82.7	2.2	39.8	1.8237
1 : 1 (mol %)			4.1	21.4	73.9	2.2	39.7	1.8237
3 : 1 (mol %)	22.2	3.9	4.5	19.4	26.5	2.2	39.8	1.9823
A8-A20								
1 : 1 (mol %)	19.5	4.5	4.1	21.5	60.4	2.2	39.6	1.8391
	16.7	5.2						
A8-A22								
1 : 1 (mol %)	20.2	4.7	4.1	21.3	74.7	2.2	40.5	1.8834
	13.0	6.7	3.8	23.1				
A8-A24								
1 : 1 (mol %)	20.1	3.5	4.1	21.2	131.6	2.2	41.6	1.9305
			3.7	23.4				

<sup>a</sup> Figures in A8, PA8, etc., refer to the carbon number of the acrylate; PEHA, poly(2-ethylhexylacrylate).

<sup>a,b</sup> Ref. 30.

other than those resulting from simple atomic contact. These have sufficient regularity (order) and lead to one or more discrete scattering peaks of sufficient intensity, similar to those described by Muller.<sup>21</sup> Other intersegmental contributions to scattering patterns smaller than VDW occur at higher angles, viz.,  $45^\circ$ ,  $d = 2.2$  Å. Among other prominent features observed in the diffractograms were the following:

- (i) For polymers and copolymers having up to 12 methylene groups in the side chain, a wide halo appeared at  $19^\circ$  and  $d = 4.6$  Å.
- (ii) In contrast to the acrylate homopolymers, up to  $n$ -C<sub>18</sub> copolymers of  $n$ -C<sub>18</sub>-C<sub>24</sub> acrylate with  $n$ -C<sub>8</sub> acrylate showed a well-defined peak at  $21^\circ$ ,  $d = 4.17$  Å.
- (iii) In the poly(C<sub>8</sub>-co-C<sub>18</sub> acrylate), a  $19^\circ$  halo appeared along with the  $21^\circ$  peak. The prominence of a halo over a peak or vice versa around  $20^\circ$  has been observed to be influenced by changes in the copolymer composition. The spacing of 4.17 Å corresponds to the typical hexagonally packed cylinders of  $n$ -alkane crystals close to their melting points.<sup>21</sup> The hexagonal packing limits the minimum dis-

tance between adjacent pendants to 4.82 Å. As the maximum distance between the two adjacent side chains belonging to contiguous monomeric units in the extended zigzag form of

**Table II Effect of Different Polymers at 400 ppm Concentration on the Pour Point ( $12^\circ\text{C}$ ) of a Typical Indian Diesel Fuel**

Polymer Designation	Pour-point Depression ( $\Delta p$ , $^\circ\text{C}$ )
PA-8	Nil
PEHA	Nil
PA-12	Nil
PA-18	3
A8-A18	
1 : 3 mol %	9
1 : 1 mol %	15
3 : 1 mol %	9
A8-A20	
1 : 1 mol %	9
A8-A22	
1 : 1 mol %	3
A8-A24	
1 : 1 mol %	Nil
Additive X	21

the main chain is 2.54 Å, it is necessary that the side chains in alternative monomer units should be on opposite sides of the main chain to fit the hexagonal packing. The probable configuration for such a structure would be one of *threo-di-syndiotactic*.

On the other hand, the side chains carrying 8–12 methylene groups do not crystallize but give a larger halo at higher angles, with  $d = 4.6$  Å corresponding to a packing of pseudo-hexagonal type. The restrictive influence of the backbone of the polymer molecule decreases with increasing pendant length of its constituent monomer(s). This was observed with the members of the  $C_{18}$ – $C_{24}$  series. A shoulder appeared with  $C_{22}$  and beyond at  $23.5^\circ$ ,  $d = 3.75$  Å. This was stated to correspond to the orthorhombic packing in polyethylene.<sup>25</sup> Our results are thus in agreement with the proposed packing model of Hsieh et al.<sup>25</sup>

Thus far, X-ray diffraction studies on waxes were either carried out with individual *n*-alkanes<sup>12</sup> or their mixtures with a narrow carbon number distribution, e.g., Chichakli's<sup>10</sup> work on  $C_{22}$ ,  $C_{26}$ – $C_{36}$ ,  $C_{32}$ – $C_{35}$ ,  $C_{38}$ – $C_{40}$ , and  $C_{50}$ – $C_{53}$  *n*-alkanes. These were crystallized from *n*-heptane. Such studies are valuable for understanding basic structural features, but are difficult to translate into practical situations where wax is a complex mixture of hydrocarbons, crystallizing from a still more complex fluid matrix. In our present work, we isolated the waxes from their natural matrix, viz., diesel fuel itself. The composition is more complex. The principal constituents (> 90%) are *n*-alkanes corresponding to the higher boiling range of the diesel fuel having a wide carbon number distribution, i.e.,  $C_9$ – $C_{33}$ . It is believed that the cold-flow properties of the waxy petroleum fluids (e.g., diesel fuel) are a consequence of separation of *n*-alkanes (wax) on cooling, the size and morphology of wax crystals separating out, and their interaction among themselves as well as with the liquid matrix. This is manifested in the form of a high cloud point, high pour point, non-Newtonian flow, high plastic and apparent viscosities, and, often, the onset of yield stress (*inter alia*, see Ref. 31).

The comb-type polymers prepared for the present study were screened for their possible wax crystal interaction by examining their effect on the pour point of a commercial diesel fuel having an initial pour point of  $12^\circ\text{C}$ . Their effect, as pour-point depression ( $\Delta p$ ), at 400 ppm concentration in the diesel oil is shown in Table II. It is observed that the homopolymers up to  $C_{12}$  and copolymers of  $C_8$  with monomers beyond  $C_{20}$  were the least effective

Table III X-Ray Diffraction Data of Additive X and Waxes Isolated from Diesel (Pour Point  $12^\circ\text{C}$ ) Under Different Conditions

Designation <sup>a</sup>	Hexagonal Packing (VDW) <sup>b</sup> $d = 4.1$ – $4.6$ Å		Long Spacing (LVDW) <sup>c</sup>				Pseudo-hexagonal (Halo) <sup>d</sup> $d > 4.6$ Å		Orthorhombic <sup>e</sup> $d = 3.5$ – $3.8$ Å		Segmental/Intersegmental Higher Angle $d = 2.2$ Å	
	$2\theta$	$d$ Å	$2\theta$	$d$ Å	$2\theta$	$d$ Å	$2\theta$	$d$ Å	$2\theta$	$d$ Å	$2\theta$	$d$ Å
Additive X	21.5	4.1					19.8	4.4				
Wax K	21.5	4.1	4.3	20.2	5.1	17.1	6.5	13.5	6.5	23.6	3.7	
Wax L	21.4	4.1	3.0	29.4	5.9	14.9	8.9	9.9	8.9	23.7	3.7	40.4
Wax M	21.3	4.1			4.8	18.2	7.2	12.8	7.2			40.1
Wax N	21.6	4.1	3.2	27.3			6.2	14.1	6.2			39.9
							6.4	13.7	6.4			
							9.3	9.5				

<sup>a</sup> Wax K isolated at  $12^\circ\text{C}$ . Wax L isolated by urea adduction (Ref. 7). Wax M isolated after doping with X at  $3^\circ\text{C}$ . Wax N is wax L + 1200 ppm X.

<sup>b-d</sup> Ref. 30.

<sup>e</sup> Refs. 32 and 33.

or had no effect at all. Maximum  $\Delta\rho$  could be achieved when a C18 pendant was present along with a short chain (spacer) in a particular mole ratio (example: PA 8 : 18, 1 : 1). This effect was further enhanced by using a complex of the polymer with an alkylbenzene. This product is under development for commercial application and is referred to as additive X in this work.

The principal characteristics of the WAXD pattern of the synthetic additive (X), the two wax samples (K and L), as well as wax-additive interaction samples (M and N) have been compiled for convenience in Table III and the diffractograms shown in Figures 4 and 5. The assignment of various peaks was in accordance with the reported literature.<sup>30,32,33</sup>

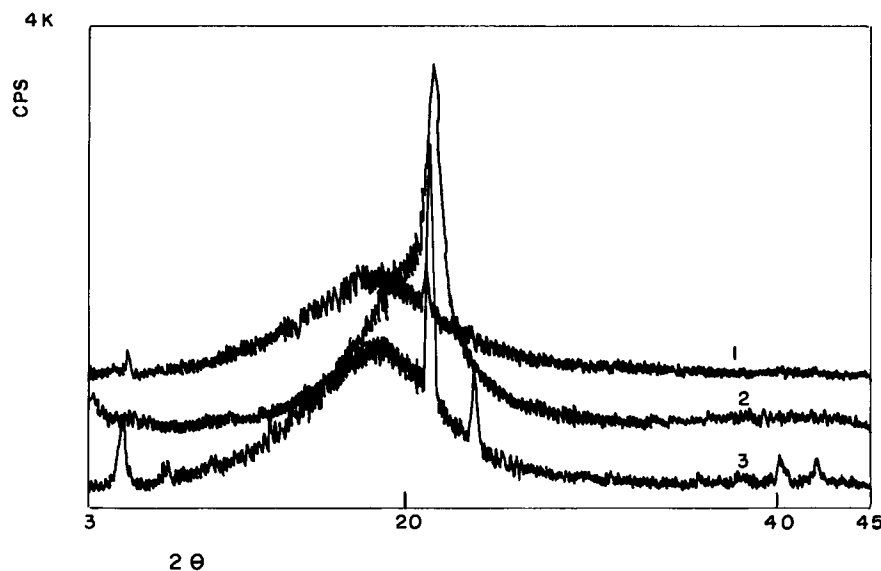
All the wax samples as well as the comb polymers showed the characteristic hexagonal packing pattern, indicated by prominent VDW peaks between  $d = 4.1$  and  $4.6 \text{ \AA}$ . There are major departures with respect to the LVDW peaks and other modes of crystal packing (pseudo-hexagonal appearing as halo  $d > 4.6 \text{ \AA}$ , orthorhombic  $d = 3.5\text{--}3.8 \text{ \AA}$ , and segmental/intersegmental reflections). Wax K has a prominent halo ( $18.8^\circ$ ,  $d = 4.69 \text{ \AA}$ ) similar to that present in the additive X (see column 3). However, wax K has a number of peaks identified as LVDW or long spacing (i.e.,  $4.36^\circ$ ,  $5.15^\circ$ , and  $6.54^\circ$ ) as well as those arising from orthorhombic packing ( $23.6^\circ$ ,  $d = 3.75 \text{ \AA}$ ), which are absent in X.

The corresponding *n*-alkane concentrate (sample

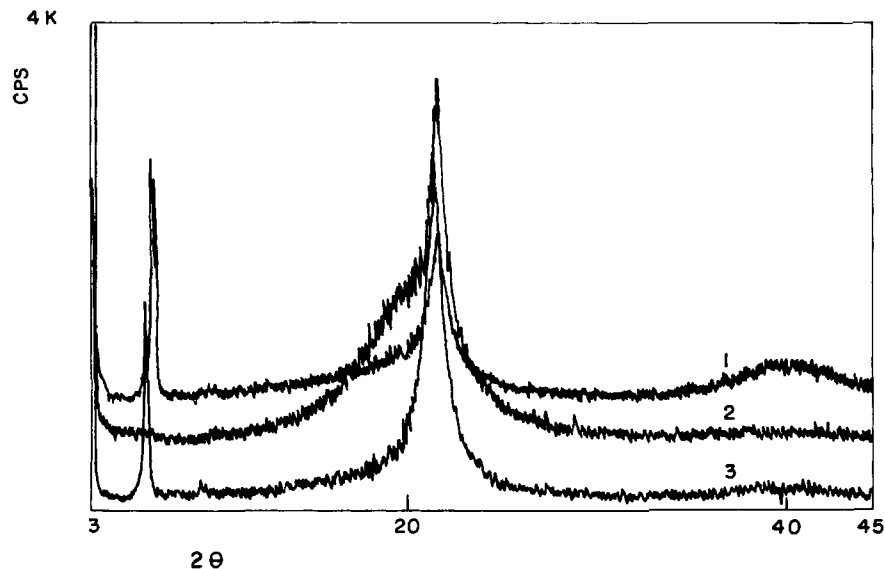
L) displayed LVDW peaks differing in position from those of sample K. It is also devoid of peaks corresponding to pseudo-hexagonal (halo) as well as orthorhombic packing, in sharp contrast to wax K. Another prominent feature of wax L is the presence of a high-angle peak ( $40.4^\circ$ ,  $d = 2.22 \text{ \AA}$ ) that is absent in both X and K. The diffraction pattern of wax M is similar to that of wax K except for the presence of higher angle peaks (at  $40.15^\circ$ ,  $42.15^\circ$ ,  $d = 2.24$  and  $2.14 \text{ \AA}$ ), respectively (absent in both X and K, but present in L). The higher-angle peaks are arising quite likely from the extended chains and will be commented upon in a future communication. Although a number of LVDW peaks are present, their precise positions are different from those in wax K, there being a general shift toward higher angles.

This shift could reflect the influence of the additive X on the crystal habit of the wax. It may be noted that the pour point of the diesel oil was depressed by  $21^\circ\text{C}$  by X at this dose (400 ppm, Table II).

Wax N is a mixture of L with 1200 ppm of X. Its diffraction pattern closely resembles that of L inasmuch as the pseudo-hexagonal halo as well as orthorhombic packing are absent in both. The LVDW peaks showed a general shift toward higher angles. The most characteristic feature is a split at  $6.25^\circ$ ,  $d = 14.1 \text{ \AA}$ . If the two components formed a eutectic, the features of both components would be expected. However, there is no evidence of the pseudo-hexa-



**Figure 4** WAX diffractograms of (1) wax from diesel obtained on cooling (wax K); (2) additive X; and (3) wax isolated from diesel containing additive X (400 ppm) at  $0^\circ\text{C}$  (wax M).



**Figure 5** WAXD patterns of (1) wax isolated from diesel containing additive X (1200 ppm) (wax N); (2) additive X; and (3) wax isolated from diesel by urea adduction method.

gonal halo in N, which is a prominent feature of X. It is therefore suggested that there is a strong interaction between X and L in the solid state, perhaps due to cocrystallization resulting in the two distinctive features in the WAXD pattern.

Chichakli<sup>10</sup> concluded from his studies that the additive turns the vertically oriented paraffin molecules to the horizontal position in the wax crystals. This results in turning the crystal layers on their thin edges, giving an impression of a needle-shaped habit. The additive, according to Chichakli, adheres to the surface of the crystals only. Our studies indicate that the interaction of the additive with the wax is of a deeper nature, perhaps indicating cocrystallization, as mentioned above. There are some features in the wax isolated by cooling the diesel oil that are present neither in the additive nor in the *n*-alkane concentrate (sample L). These peaks ( $23.5^\circ$ ,  $d = 3.73 \text{ \AA}$ ) have been assigned to the orthorhombic packing by earlier workers. Their origin and significance will be reported later.

## CONCLUSION

Wax crystals isolated from waxy petroleum distillates (diesel fuels) are basically hexagonal with some features relating to mal-structures. This feature is shared with synthetic comb polymers with more than eight carbons in the side chain. The origin of peaks corresponding to orthorhombic packing and

segmental reflections needs to be explained. The comb polymers that are effective pour-point depressants result in distinctive changes in the diffraction pattern of the LVDW peaks, which show a general shift to higher angles and, in some cases, a distinct split.

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