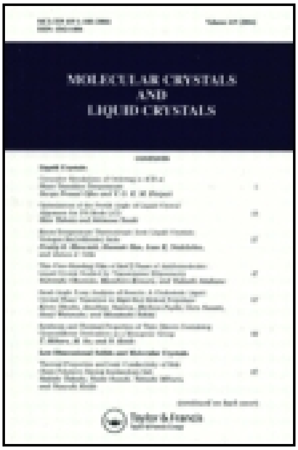

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Thermal and Structural Study on Liquid-Crystalline Phase Transitions in bis-Alkyl Trimethyl Ammonium Dichromates

Nathalie Fossé [a] , Jean Yves Mevellec [b] & Luc Brohan [a]

[a] Institut des Matériaux Jean Rouxel, UMR CNRS N′ 6502 Laboratoire de Chimie des Solides 2, rue de la Houssinière. B.P. 32229, 44322, NANTES, Cedex, 03, FRANCE

[b] Institut des Matériaux Jean Rouxel, UMR CNRS N° 6502 Laboratoire de Physique Cristalline, 2, rue de la Houssinière. B.P. 32229, 44322, NANTES, Cedex, 03, FRANCE

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Thermal and Structural Study on Liquid-Crystalline Phase Transitions in bis-Alkyl Trimethyl Ammonium Dichromates

NATHALIE FOSSÉ[a], JEAN YVES MEVELLEC[b] and LUC BROHAN[a]

[a]*Institut des Matériaux Jean Rouxel, UMR CNRS N° 6502 Laboratoire de Chimie des Solides 2, rue de la Houssinière. B.P. 32229, 44322 NANTES Cedex 03 – FRANCE. and* [b]*Institut des Matériaux Jean Rouxel, UMR CNRS N° 6502 Laboratoire de Physique Cristalline. 2, rue de la Houssinière. B.P. 32229, 44322 NANTES Cedex 03 – FRANCE*

A series of bis-alkyltrimethylammonium dichromates $(C_nH_{2n+1}(CH_3)_3\,N)_2\,Cr_2O_7\bullet \times H_2O$ (where n = 8, 10, 12, 14, 16, 18, and $0\leq x\leq 2$) compounds (ATMACr) was synthesized from alkyltrimethylammonium bromide and $K_2Cr_2O_7$. The phase transitions and mesogenicity of these substances were studied by X-ray diffraction, DSC measurements, and FT-IR observations. In the series of hydrated ATMACr compounds, the decreasing of the $\Delta S_{Sm\text{-}I}$ phase transition values with the alkyl chain length n increase, suggest that the disorder in the smectic A phase is dependent on the carbon. From the temperature dependence of DTMACr IR spectra, the increase of the CH_2 stretching vibrations frequency and the bandwidth accompanied by a lowering of the peaks intensity can be ascribed to the introduction of a high degree of conformational and motional disorders into the alkyl chain.

Keywords: hydrated and anhydrous alkyltrimethylammoniumdichromates; liquid-crystalline phase transitions

INTRODUCTION

Recently, a soft chemistry route has been successfully used to prepare mesostructured bis-alkyltrimethylammonium-dichromates (ATMACr) with n = 12, 14, 16, 18 [1] [2] and bis-dialkyldimethylammonium-dichromate with n = 16 [3]. The stacking parameter of these lamellar compounds obviously depends on the length of alkyl chain and on the water molecules content. Among them, two hydrated and one anhydrous crystalline forms of bis-octadecyltrimethylammonium dichromate (OTMACr) have been isolated and characterised by means of TG-DSC-MS and XRPD. The crystal structure of the anhydrous bis-octadecyltrimethylammonium dichromate consists of discrete dichromates that stack in a layered order separated by a double layer of octyltrimethylammonium surfactant chains (Fig. 1).

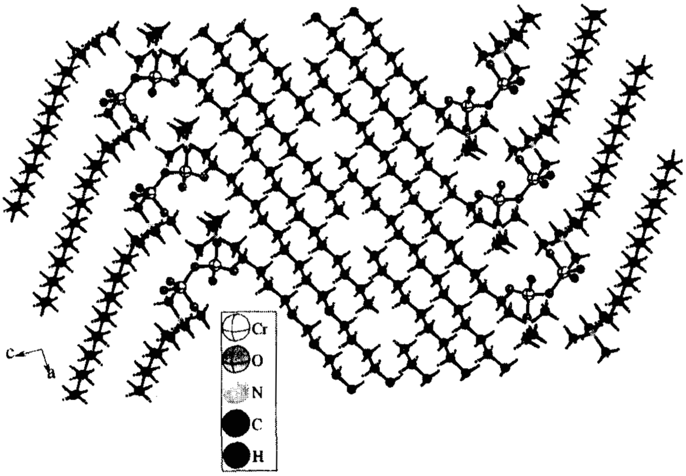


FIGURE 1 Packing of the dichromate clusters and octadecyltrimethylammonium cations viewed in projection along the b axis.

The structural conformation of the $Cr_2O_7^{2-}$ anions is strongly correlated to the charge and size of the A cation in the $A_2Cr_2O_7$ compounds. So, viewed along the Cr-Cr direction, the two $[CrO_4]$ tetrahedra, sharing the bridging oxygen atom exhibit a staggered conformation when A = $(CH_3)_4N^+$, $(C_nH_{n+1}(CH_3)_3N^+$, while an eclipsed conformation is observed for spherical cation, A = K^+, Rb^+. The detailed conformation and molecular packing of the compounds determined from single crystal X-ray diffraction data analysis will be published elsewhere [4].

In this paper, investigations on the phase transitions of bis-alkyltrimethylammonium dichromates $(C_nH_{n+1}(CH_3)_3N)_2Cr_2O_7{\bullet}2H_2O$ with n = 12, 14, 16, 18 are reported on the basis of DSC measurements, X-ray diffraction and FT-IR data. The effects of the alkyl chains length and the water molecules content on the phase transitions in the ATMACr series are discussed.

EXPERIMENTAL

A solution of $K_2Cr_2O_7$, $C_nH_{2n+1}(CH_3)_3NBr$ (ATMABr) and H_2O in a 1:2:100 molar composition was heated at 80°C for 12 hours, in a screw top tube. After cooling, the solid orange product was recovered by filtration, washed with distilled water and dried in air at room temperature or at 100°C.

The phase transitions and mesogenicity were studied by DSC measurements using a SETARAM instruments DSC 121, at a heating/cooling rate of 2 K min^{-1} in a temperature range 298 K - 500 K. The temperature dependence of the IR spectra was measured for KBr disks by a Perkin Elmer 1760X Fourier Transform spectrometer equipped with a hot stage, in the wavenumber range 4000 cm^{-1} - 600 cm^{-1}. The temperature control of the sample was monitored by a alumel-chromel thermocouple. X-ray powder diffraction (XRPD) patterns were recorded on a D5000 SIEMENS diffractometer in a Bragg-Brentano geometry using CuK_α radiation, with a 2θ step width of 0.03° and a step time of 1.5 s.

RESULTS AND DISCUSSION

Structural characterization:

As the most common packing structure observed in surfactant-water system, the alkyltrimethylammonium chromates adopts a bilayer configuration in which the hydrocarbon chains are extended away from the planes containing the dichromate groups (Fig.1). Therefore layered structure is composed of an alternating arrangement of an inorganic wall, $(Cr_2O_7)^{2-}$ and organic bilayer. In the anhydrous and hydrated ATMACr, the interlayer spacing, smaller than the expected value for the fully extended molecular model is achieved through a tilting of the surfactant chains of about 70.5° and 75.6° respectively, from the normal to the $(Cr_2O_7)^{2-}$ plane [1] [2].

Phase transitions study in OTMACr

The temperature dependence of X-ray powder diffraction patterns of OTMACr between 2θ = 1.5 and 16° is shown in figure 2. This scattering angle region correlates with an interlayer spacing. Unfortunately, and under the experimental conditions used, an anhydrous bis-octadecyltrimethylammonium-dichromate parasitic phase appears beside the smectic phase (Sm) at 75°C.

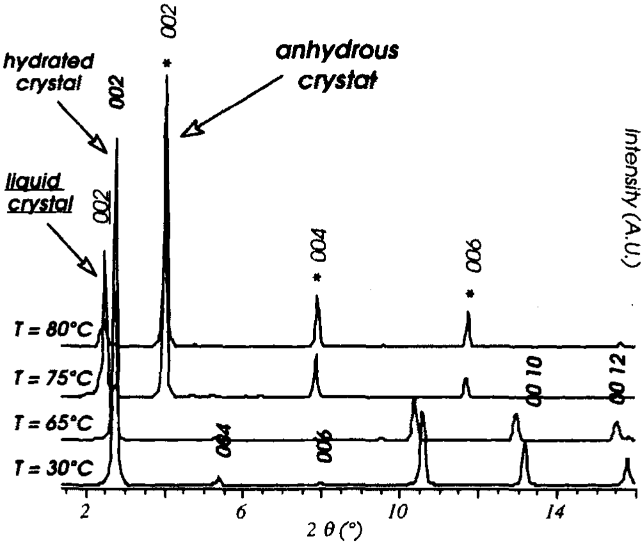


FIGURE 2 In situ, thermal XRPD study of hydrated OTMACr showing the Solid-Mesophase transition

From the d_{00l} peaks positions, the interlayer spacing is evaluated to be 33.19 Å at T = 30°C. These peaks shift to a lower 2θ direction above 65°C, reflecting a solid-mesophase transition deduced from the DSC curves and polarizing microscope observations. The diffraction intensity decreased drastically and the interlayer spacing of the smectic A phase is calculated to be 37.05 Å at T = 75°C. The temperature dependence of the d_{002} spacing and the Full Width at Half-Maximum (FWHM) deduced from the X-ray diffraction data is shown in (Table I).

TABLE I Thermal evolution of d_{002}-spacing and Full Width at Half-Maximum (FWHM) in $(C_{18}H_{37}(CH_3)_3N)_2Cr_2O_7 \cdot 2H_2O$.

Temperature (°C)	d_{002} (Å)	FWHM of *002* (Å)
30	33.19	0.108
65	33.41	0.126
75	37.05	0.096
80	37.32	0.162

In the crystalline domain (30°C < T < 65°C), the d_{002} spacing and the Full Width at Half-Maximum (FWHM) increase due to thermal expansion of the crystalline lattice and thermal disorder of the alkyl chains, respectively. At 75°C, the Sm phase appears, the interlayer spacing increase by about 4 Å while a narrowing of the FWHM is observed. The solid-mesophase transition is known to result not only from a loss of rotational or translational order, but also from a phenomenon of chain melting (conformational disorder of the alkyl chains). The increase in d_{002} probably results from a lower tilt of the alkyl chains in the layer and the increase of the coherence length is consistent with a relaxation of the alkyl chains during the rotational motion or melting chain phenomenon. Above the S/Sm transition temperature, the peaks become broad, reflecting a loss of packing regularity in the crystalline lattice.

Effect of alkyl chain length on the Phase Transitions in ATMACr

As previously reported and according to the hydrated or anhydrous nature of the compounds the D.S.C. curves exhibit two or one endothermic transitions during the heating process and for T<180°C [2].

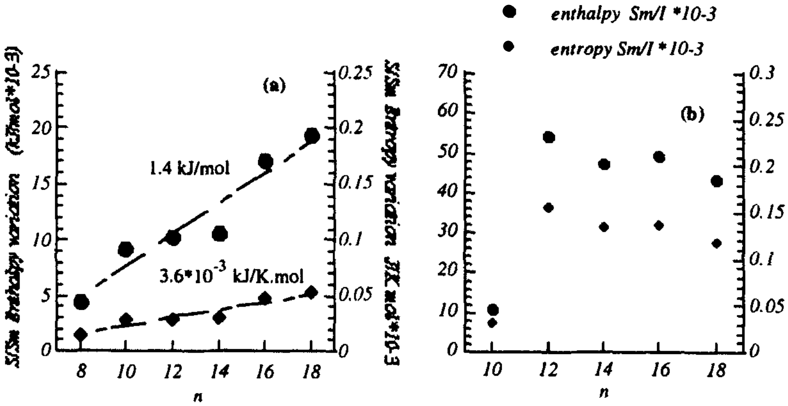


FIGURE 3 Thermodynamic parameters of hydrated ATMACr: (a) $\Delta H_{S\text{-}Sm}$ and $\Delta S_{S\text{-}Sm}$ enthalpy and entropy of transition from S to Sm; (b) $\Delta H_{S\text{-}Sm}$ and $\Delta S_{S\text{-}Sm}$ enthalpy and entropy of transition from Sm to Isotropic liquid.

The dependence of S-Sm, Sm-I phase transitions enthalpies and entropies on the alkyl chain length (*n*), in the hydrated ATMACr is shown in figures 3 (a) and (b). The $\Delta H_{S\text{-}Sm}$ (and $\Delta S_{S\text{-}Sm}$) values continuously increase of about 1.4 kJ/mol (and 3.6 J/K.mol) when the number, *n*, of methylene groups in the spacer segment is increased. The mesophase was identified as smectic A by the appearance of characteristic focal conic textures [2][5], consistent also with the recorded values of the isotropization enthalpies ($\Delta H_{Sm\text{-}I}$ = 54 - 43 kJ/mol) and entropies ($\Delta S_{Sm\text{-}I}$ = 160 - 120 J/K.mol). The values of the

Sm-I phase transition entropies, slightly decrease with an increase in the alkyl chain length and suggest that the disorder in the smectic A phase is dependent on the carbon number. However, one notes that the ΔH_{Sm-I} and ΔS_{Sm-I} values were smaller for the lower homologue $n = 10$, which suggests that the smectic A phase is characterized by a different structural order. A possible monolayer smectic A structure could be detected for hydrated

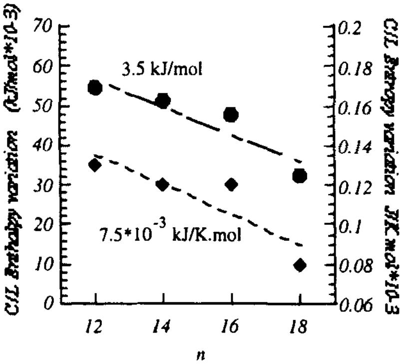


FIGURE 4 Thermodynamic parameters of anhydrous ATMACr: $\Delta H_{C\text{-}L}$ and $\Delta S_{C\text{-}L}$ enthalpy and entropy of transition from Crystal to Liquid.

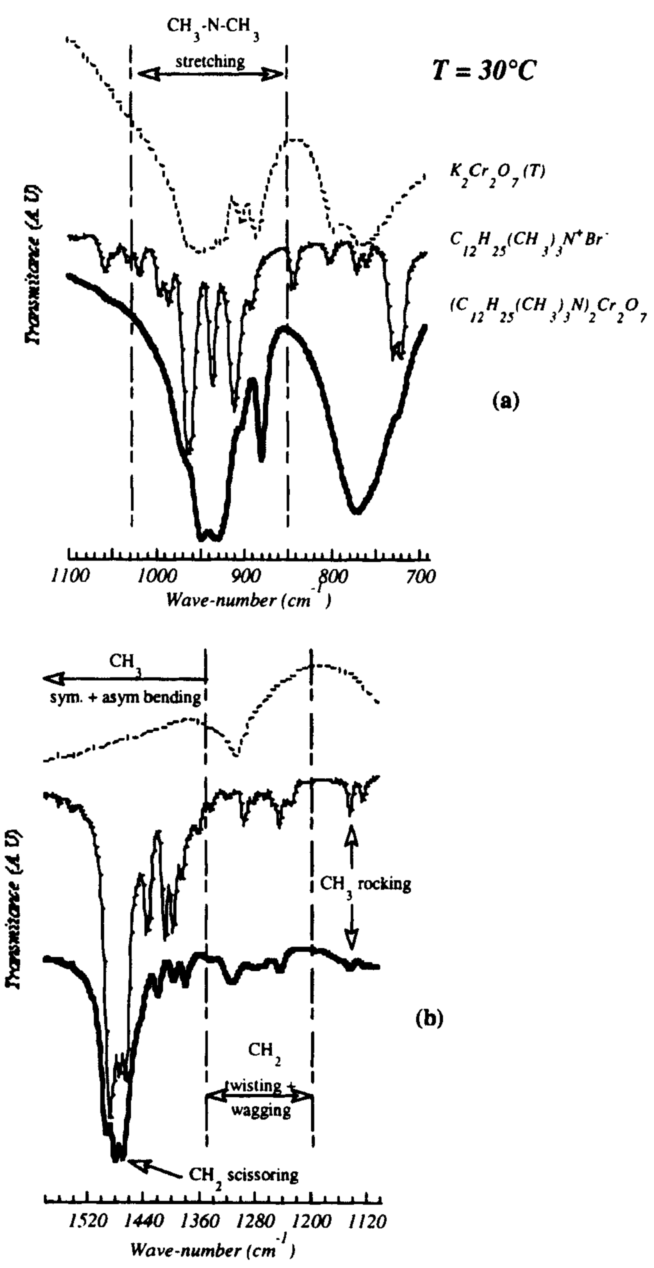
No mesomorphic phase was found for the anhydrous ATMACr in the polarizing microscope observations and the crystal transformed directly to the isotropic liquid phase. As shown in figure 4, the associated C/L enthalpies and entropies are close to the values observed for the homologue hydrated phases (figure 3 (b)).

Phase transitions and vibrational spectra of hydrated DTMACr (n = 12)

Before to investigate the thermal behaviour of the bis-dodecyltrimethylammonium dichromate (DTMACr) by mean of IR measurements, the spectra of parent phases have been recorded at room temperature. Obviously, the DTMACr IR spectrum (figure 5) results from a superposition of $Cr_2O_7^{2-}$ and dodecyltrimethylammonium cation spectra. Between 700 to 1000 cm^{-1} (figure 5 a), the IR spectrum of DTMACr results in an overlap of each other.

The same behaviour is also observed in the wave-number region 1200-1360 cm^{-1} (figure 5 b) while the $Cr_2O_7^{2-}$ contribution to the IR spectra can be considered as totally insignificant in wave-number range 2700-3200 cm^{-1} (figure 5 c).

The DTMACr IR spectra analysis may be performed by distinguish the polar and the alkyl chain contributions. The bands characteristic of polar head group are detected in the wave-number region between 900 - 1020 cm^{-1} and 3000 - 3070 cm^{-1}. The CH_3 asymmetric stretching and CH_3-N^+-CH_3 stretching vibrations are located near 3030 cm^{-1} and 850-1030 cm^{-1}, respectively. The temperature dependence of the peak frequency of these bands is shown in figure 6. The CH_3 asymmetric stretching peak enlarges and shifts to the lower frequency on increasing temperature. When the temperature reaches the Solid - Smectic (S-Sm) phase transition point the band width increases dramatically. The CH_3 asymmetric stretching vibration continuously shifts from 3032 to 3028 cm^{-1} at T=146°C, which corresponds to the Sm-I phase transition temperature.


CH_3-N-CH_3
stretching
T = 30°C
$K_2Cr_2O_7$ (T)
$C_{12}H_{25}(CH_3)_3N^+Br^-$
$(C_{12}H_{25}(CH_3)_3N)_2Cr_2O_7$
Transmittance (A.U)
(a)
1100
1000
900
800
700
Wave-number (cm^{-1})
CH_3
sym. + asym bending
CH_3 rocking
Transmittance (A.U)
(b)
CH_2
twisting +
wagging
CH_2 scissoring
1520
1440
1360
1280
1200
1120
Wave-number (cm^{-1})

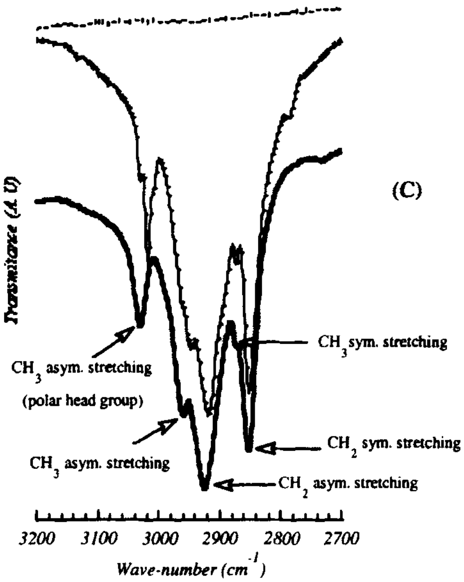


FIGURE 5 showing the $Cr_2O_7^2$, dodecyltrimethylammonium group and hydrated DTMACr IR spectra recorded at T= 30 ° C between: a) 700 and 1100 cm^{-1}, b) 1100 and 1580 cm^{-1}, c) 2700 and 3200 cm^{-1}.

The CH_3-N^+-CH_3 stretching vibrations shows a temperature dependence similar to that of the CH_3 asymmetric stretching mode. When increasing temperature, the CH_3-N^+-CH_3 stretching vibrations change the position from 948 and 932 cm^{-1} to 944 and 934 cm^{-1} at $T_{(S\text{-}Sm)}$ and to 937 cm^{-1} at $T_{(Sm\text{-}I)}$. Figure 5 shows the characteristic bands of alkyl chains detected in the wave number region between 700 and 3200cm^{-1}. The CH_2 rocking vibration is located near 720 cm^{-1} (Figure 5 a). The CH_3 rocking and bending (symmetric and asymmetric modes) vibrations appear at about 1142 cm^{-1} and in range 1360 - 1520 cm^{-1}, respectively (Figure 5 b).

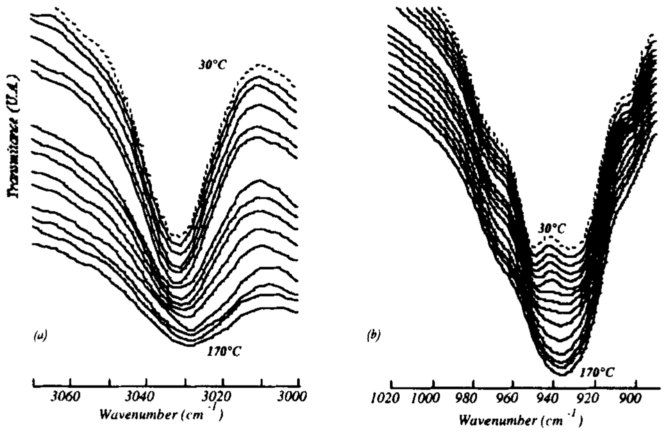


FIGURE 6 Temperature dependence of hydrated DTMACr IR spectra showing: a) CH_3 asymmetric stretching vibrational frequencies of the polar head group (3030 cm^{-1}) and b) CH_3-N^+-CH_3 stretching (850-1030 cm^{-1}).

The series of sharp bands between 1200 and 1350 cm^{-1} contain the CH_2 twisting and wagging vibrations while the CH_2 scissoring mode appears at 1468 cm^{-1}. The broad bands between 2700 and 3000 cm^{-1} in the spectrum shown figure 5c, are due to asymmetric and symmetric stretching of the hydrocarbon chain. As commonly observed for compounds containing extended methylene chains, in this wave numbers range, the strong bands are due to the antisymmetric (2924 cm^{-1}) and symmetric (2853 cm^{-1}) CH_2 stretching modes and the weak bands to the antisymmetric (2962 cm^{-1}) and symmetric (2872 cm^{-1}) CH_3 stretching modes. The variation in temperature of the peaks frequency of these bands is shown in figures 7 and 9. The CH_2 and CH_3 stretching vibrations shift to the higher frequency on increasing temperature. When the temperature reaches the Solid-Smectic phase transition, the bandwidth of the peak and the frequency increase. As shown figure 8, the CH_2 symmetric stretching vibration continuously increases from 2852 to 2854 cm^{-1} between $T_{(S\text{-}Sm)}$ and $T_{(Sm\text{-}I)}$ while the asymmetric stretching mode abruptly changes the position from 2924 to 2926 cm^{-1} at $T_{(S\text{-}Sm)}$ and to 2928 cm-1 at $T_{(Sm\text{-}I)}$. Above the $T_{(S\text{-}Sm)}$ transition, a decreasing of the peak intensity and an enlargement of the bandwidth are observed when increasing temperature.

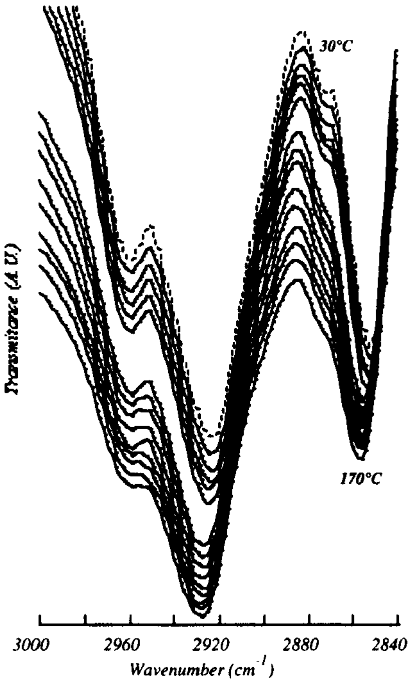


FIGURE 7 Temperature dependence of IR spectra between 2840 and 3000 cm^{-1} of hydrated DTMACr.

The combination of the increase in the frequency and the bandwidth accompanied by a lowering of the peaks intensity can be ascribed to the introduction of a high degree of conformational and motional disorders into the alkyl chain [6-10].

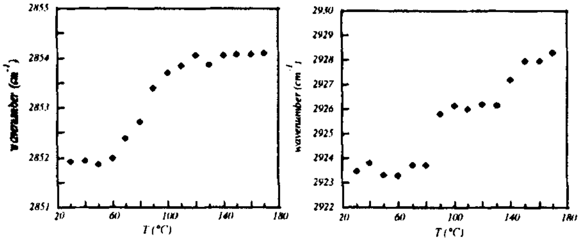


FIGURE 8 Temperature dependence of CH_2 stretching vibrational frequencies in DTMACr: a) symmetric and b) asymmetric modes.

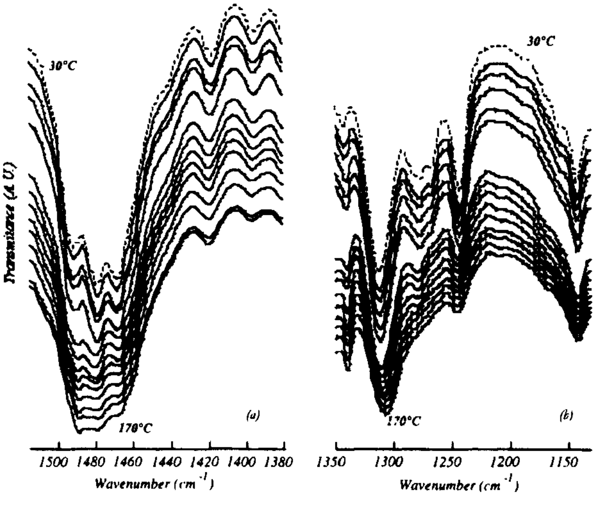


FIGURE 9 Temperature dependence of IR spectra in DTMACr, showing: a) the CH_2 symmetric and asymmetric bending (1360-1520 cm^{-1}) and the

CH_2 scissoring (1468 cm^{-1}); b) CH_3 rocking (1142cm^{-1}), CH_2 twisting and wagging (1200-1350 cm^{-1}).

The change of the CH_2 stretching vibrations at the S-Sm transition can be explained both to the change in the geometry of the alkyl chains packing and to the increase in the force constants of CH_2 bonds, in other words, to the softening of the rigidity of the alkyl chain packing. Confirmation of this conclusion comes from the further decrease in the frequency of the CH_2 scissoring band at 1468 cm^{-1} and increase in the bandwidth as shown on the figure 9 a.

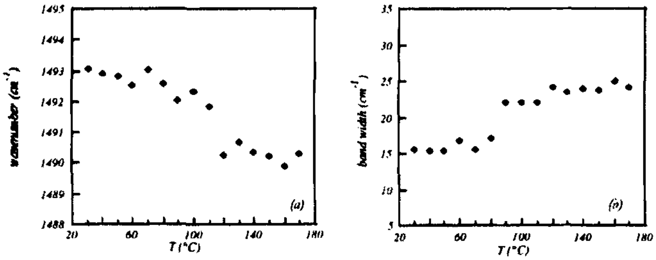


FIGURE 10 Temperature dependence of CH_3 bending: a) vibrational frequencies and b) band width in DTMACr.

Indeed, the CH_2 scissoring mode is very sensitive to changes in the chain packing arrangements and to the intramolecular interactions [6].

The temperature dependence of CH_3 bending peak frequency and bandwidth is shown in figure 10. The frequency of this band decreases continuously from 1493 to 1490 cm^{-1} between $T_{(S\text{-}Sm)}$ and $T_{(Sm\text{-}I)}$ while the bandwidth abruptly enlarges of about 7 cm^{-1} at $T_{(S\text{-}Sm)}$. In the temperature region above this transition point, the bandwidth increases slowly.

CONCLUSION

Hydrated and anhydrous chromium oxides incorporating alkyltrimethylammonium cations of different length were prepared. No mesomorphic phase was found for the anhydrous ATMACr in the polarizing microscope and DSC observations and the crystal transformed directly to the isotropic liquid phase. The hydrated one has been found to exhibit a smectic A phase on the basis of study by using RX, DSC, and IR analysis. The decreasing of the ΔS_{Sm-I} phase transition values with an increase in the alkyl chain length suggest that the disorder in the smectic A phase is dependent on the carbon number. At the S/Smectic A phase transition of the hydrated OTMACr, the increasing of the interlayer spacing results from a lower tilt of the alkyl chains relative to the normal of the Cr_2O_7 layer. Above the S/Sm transition temperature, the X-ray diffraction peak broadening in OTMACr, reflects a loss of packing regularity in the crystalline lattice. In DTMACr, the change of the CH_2 stretching vibrations at the S-Sm transition can be explained both to the change in the geometry of the alkyl chains packing and to the increase in the force constants of CH_2 bonds, in other words, to the softening of the rigidity of the alkyl chain packing. The initiation of the chain melting phenomenon (conformational disorder into the alkyl chains) at $T_{(S-Sm)}$, is reflected in the infrared spectra by a shift to the lower frequency of the CH_2 scissoring mode and an abrupt increase in the bandwidth.

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