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Polymer 40 (1999) 3901–3908

polymer

FTIR-Raman spectroscopy of polydiacetylenes with chiral pendent groups

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Received 15 April 1998; received in revised form 20 July 1998; accepted 4 August 1998

Abstract

The FTIR-Raman spectra of polydiacetylenes with chiral pendent groups ($-(CH_2)_nOCONHC^*H(CH_3)Ph$; $n = 2,3,4,6$ and 9; nR(S)MBU) were measured for samples as polymerised, cast from solution and precipitated on filter paper. Peaks due to the $-C{=}C-$ and $-C{\equiv}C-$ backbone stretching vibrations occur above 1400 cm^{-1}. A series of peaks due to the interaction of backbone and $-(CH_2)_n-$ vibrations, which reflect the structure of the alkyl chains in the pendent groups, lie between 700 and 1400 cm^{-1}. Comparison with the spectra of the related *n*-butoxy-carbonylmethylurethane sidegroup polymers (nBCMU) shows that, with the exception of 9R(S)MBU polymers, the alkyl chains of the nR(S)MBU polymers do not adopt a single conformation even in the as-polymerised samples. This is a consequence of the steric hindrance of the bulky chiral unit at the end of the pendent groups. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Raman spectroscopy; Polydiacetylene; Chiral polymers

1. Introduction

Polydiacetylenes (PDAs) exhibit intense resonant-Raman spectra that are sensitive to the structure and environment of the conjugated polymer chain [1]. Resonant-Raman scattering of the polymer chains in polymerising diacetylene monomers has been used to study the solid-state polymerisation process and the structure of both monomer crystals and the resulting polymer [2–6]. The shifts in the frequencies of the backbone bond-stretching vibrations due to the strain produced by extension of single crystal fibres [7] and the application of pressure to single crystals [8] have been measured. The precise nature of the frequency–strain relationship has enabled PDAs to be used to determine the strain in fibres in model composites using either single crystal fibres [9] or more complex copolymers [10]. The frequencies of the backbone vibrations of the extended PDA polymer chains in single crystals have negligible dispersion as a function of excitation wavelength. However, where the polymer chains occur in a variety of conformations, i.e. in heavily deformed single crystals, solutions and films cast from solution, there is a large dispersion in the resonance regime [11–15]. The soluble PDAs with *n*-butoxycarbonylmethylurethane sidegroups (nBCMU, see Fig. 1) have been used extensively in these studies. The production of ordered polymer chains in nBCMU solutions by either the addition of a non-solvent or cooling [12,16] has also been studied by Raman spectroscopy.

Although Fourier transform infrared (FTIR) Raman spectrometers are now common, relatively few reports of the FTIR-Raman spectra of PDAs have appeared [17–20]. Despite an excitation wavelength of 1.064 micron, the Raman spectrum is still dominated by the polymer backbone vibrations and even the weaker peaks, visible in the 100 to 800 cm^{-1} region, grow in intensity during the polymerisation process [19]. This is not due to resonant-Raman scattering but is a consequence of the fact that the coupling of the π-electron system with the molecular vibrations is the principal mechanism contributing to the scattering [20,21]. Hence, the FTIR-Raman spectra are dominated by the vibration modes of the polymer backbone and those in the pendent groups that couple significantly with the backbone.

The nR(S)MBUs are a class of soluble PDAs with pendent groups formed from optically pure R-(+)- or S-(−)-methylbenzyl isocyanates (Fig. 1) that are closely related to the nBCMUs. Solutions of the nR(S)MBU polymers with $n \geq 4$ have similar behaviour to those of the nBCMU polymers [22,23]. Chloroform solutions are yellow to dark orange in colour with a single, broad absorption band that is associated with worm-like polymer chains

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PII: S0032-3861(98)00618-1

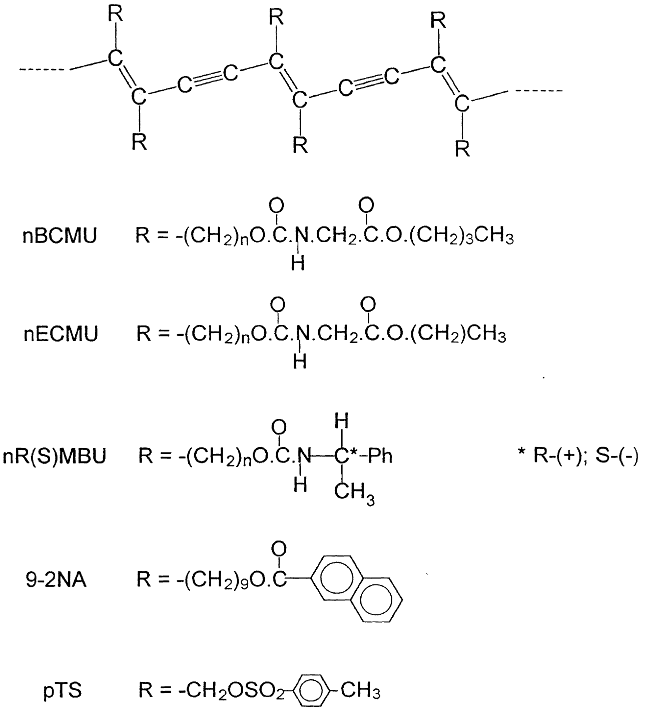

Fig. 1. Chemical structure of the polydicetylenes mentioned in the text.

[24]. Addition of a non-solvent results in the formation of ordered polymer [22]. For $n = 3$, yellow solutions are obtained only by heating; at room temperature, ordered polymer is present even in chloroform solutions [23]. The circular dichroism spectra of carefully filtered solutions containing ordered polymer and of films cast from solution show unambiguously that the polymers are pure enantiomers [22]. 9SMBU has been used to make high-quality, mono-mode optical waveguides [25] and its quadratic electro-optical coefficient has been determined by electric field modulation of 1.3 micron radiation propagating in a waveguide [26]. The nR(S)MBUs are the only example of chiral PDAs to have been reported [27]. Single crystals of sufficient size for X-ray diffraction crystallography have not yet been prepared. Even for 3BCMU and 4BCMU, the microscopic structural information obtained by X-ray diffraction for polymerised crystals has been limited by either incomplete polymerisation [28] or crystal defects [29,30]. The structural information that can be gained from optical spectrscopy is also limited [23,31,32].

As noted above, Raman spectra can provide information about the microscopic conformation of the polymer chains. For nBCMU crystals, which have been shown to have a sequence of different solid phases below the melting point [32,35], the Raman spectra show that the –C=C– and –C≡C– backbone stretching vibrations, at ca. 1480 and 2080 cm^{-1} in crystalline PDAs [1,7], move to higher frequency with increasing disorder [34,35]. At lower frequencies there are a series of bands, which result from the interaction of the in-plane deformation modes of the backbone, at ca. 950 and 1200 cm^{-1} [1,7], and in-plane modes of the alkyl chains in the pendent group. For extended all-trans alkyl chains, the peaks in this region are well resolved but they shift, broaden and weaken on heating when there is dynamic deformation of the alkyl chains. The spectra of cooled samples have a more complex spectrum in this region due to the presence of pendent groups with frozen in gauche conformers [34,35].

The presence of the bulky chiral moieties on adjacent pendent groups in the nR(S)MBUs (Fig. 1) mean that steric hindrance is likely to affect the formation of hydrogen bonds between the urethane moieties. The hydrogen-bonds formed between the pendent groups in the nBCMU PDAs have a strong influence on the microscopic structure in the solid state [29,30,32–34]. In order to obtain further information on the structure of the nR(S)MBU polymers, FTIR-Raman spectra of polymerised samples with residual monomer removed by solvent extraction, solution cast films and polymer absorbed on to filter paper were recorded. Spectra of similar samples of nBCMU polymers and the related ethyl urethane polymers, nECMU (Fig. 1), were recorded to provide reference data.

2. Experimental

2.1. Synthesis

The nR(S)MBU diacetylene monomers were prepared by the reaction of either R-(+)- or the S-(−)-methylbenzyl isocyanate with diacetylene diols with either 2,3,4,6, or 9 –(CH_2)– units adjacent to the diyne moiety. nBCMU and

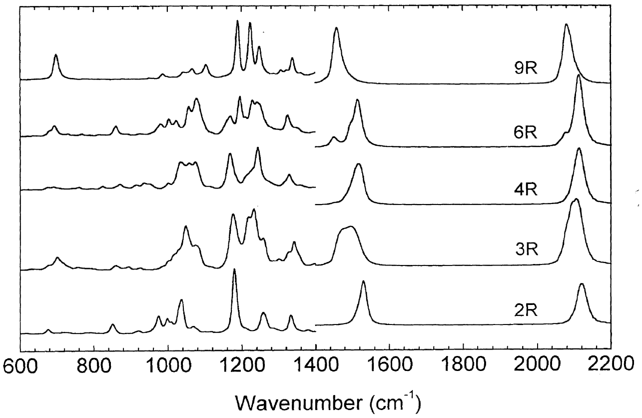

Fig. 2. FTIR-Raman spectra of as-polymerised, solvent-extracted samples of the nRMBU PDAs. From the top down: 9R, 6R, 4R, 3R and 2R. Above 1400 cm^{-1} the spectra are reduced in amplitude by a factor ca. 6.

nECMU monomers were prepared according to the literature [36]. Polymers were obtained by ^{60}Co γ-ray irradiation of micro-crystalline monomer with a dose in the range 10 to 50 Mrad. Conversion to polymer of up to 90% was obtained. Residual monomer was removed by washing with acetone prior to the recording of the FTIR-Raman spectra. Polymer films were prepared from solutions in chloroform (Merck pro analysi^{TM}). The solutions were filtered prior to either the casting of polymer films on glass substrates or absorption on to filter paper. A mechanically deformed 6BCMU samle was produced by rubbing a dry polymer sample on a glass substrate with a pad of filter paper.

2.2. FTIR-Raman spectroscopy

Spectra were recorded with a resolution of 4 cm^{-1} on a Bruker IFS 55-FRA 106 FTIR-Raman spectrometer with an Adlas 300Nd:YAG laser excitation source and a liquid-nitrogen-cooled Ge detector. In order to improve signal-to-noise ratios, the spectra were obtained by averaging between 40 and 2000 interferometer scans depending on the strength of the Raman scattering.

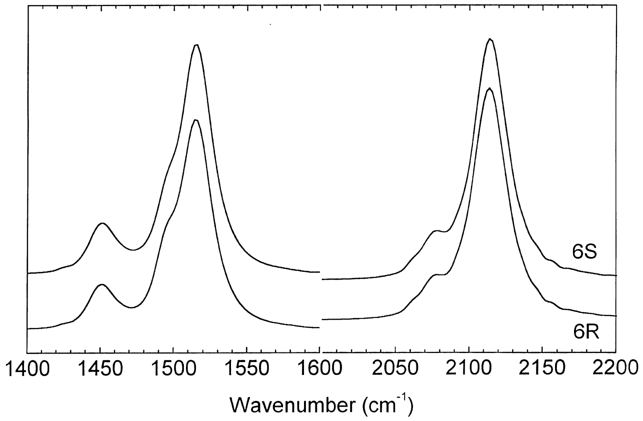

Fig. 3. Comparison of the FTIR-Raman peaks for the –C=C– and –C≡C– backbone stretching vibrations for as-polymerised, solvent-extracted samples of 6RMBU (lower spectrum) and 6SMBU (upper spectrum). Note the break in the frequency axis at 1600 cm^{-1}.

3. Results

FTIR-Raman spectra for the as-polymerised, monomer-extracted samples of the nRMBU polymers (Fig. 2) show the characteristic peaks due to the –C=C– and –C≡C– backbone stretching vibrations, between 1400 and 1500, and 2000 and 2100 cm^{-1}, respectively, and a complex, weaker structure below 1400 cm^{-1}. As noted above, the latter is due to the interaction of the in-plane deformation modes of the backbone and in-plane modes of the alkyl chains in the pendent group. The spectra of nRMBU and nSMBU polymers are essentially identical, even when the structure of –C=C– and –C≡C– stretching mode peaks is complex (Fig. 3) indicating the presence of more than one polymer chain structure in the samples. The frequencies of the Raman peaks are listed in Table 1.

Samples of as-polymerised nBCMUs (Fig. 4) have spectra with less components in the –C=C– and –C≡C– peaks and fewer, stronger peaks below 1400 cm^{-1} than for the chiral polymers. The spectrum of 4BCMU is that for a thin single crystal [37]. 6ECMU has single, sharp peaks above 1400 cm^{-1}, otherwise the spectrum is indistinguishable from that of the equivalent nBCMU polymer (Fig. 5). Observed frequencies for a selection of samples are listed in Table 2; these are generally within 1–2 cm^{-1} of the values determined in the resonant scattering regime [34,35,38], but can differ by up to 5 cm^{-1}.

The frequencies of the –C=C– and –C≡C– backbone stretching vibrations are generally shifted to higher frequency when the polymers are disordered. The peaks below 1400 cm^{-1} weaken and have a more complex structure than for the as-polymerised samples. The most disordered samples, which are prepared by rapid evaporation of the solvent on glass and filter paper and mechanical deformation, have weak, quasi-continuous spectra below

Table 1
FTIR-Raman frequencies for as-polymerised, solvent-extracted samples (*) and films cast from chloroform solution (-cast) of the nR(S)MBU chiral polydiacetylenes. Measured frequencies are identical for the R and S enantiomers except for 9S where traces of disordered polymer were present in the nominally as-polymerised sample. Frequencies are in cm^{-1} with an accuracy of 2 cm^{-1}. Relative strength is indicated by: vs, very strong (bold); s, strong (underlined); m, medium; w, weak; sh, shoulder and vw, very weak (italic)

2R(S)*	3R(S)*	4R(S)*	6R(S)*	9R(S)*	3R-cast	6R-cast	9R-cast
2119vs	**2106vs**	**2114vs**	**2114vs**		2112s	**2116vs**	**2104vs**
	2094vs		2078s	**2080vs**	**2093vs**		
	2078sh				2078sh		
1529vs		**1518vs**	**1515vs**			**1518vs**	**1495vs**
	1496vs		1494sh	**1458vs**	1496s		1470vs
	1477vs		1451s		**1496vs**		
1380vw				*1359vw*			
	1342w	*1358vw*	*1348vw*	1337m		1340w	1357vw
1333m	*1326vw*	1328w	1324w	*1322vw*	1324w	1329w	1333w
	1300vw			*1306vw*			1306w
				1286vw			
1284vw							
1257m	1257w				1257w	1250w	
	1232m	1243m	1241m	1247m		1232w	1244w
1208vw	1219w		1228m	1223s	1216m	1223w	1224m
1178s	1176m		1195m	1189s	1176m		1190m
1116vw		1168m	1168w			1155w	
1068w	1074w	1074m	1078w	1103w	1080w	1070m	1095w
		1058w	1056w	1066w			1064w
1035m	1049m	1035m	1022w	1042w	1049w		1041w
1008vw	*1029vw*				*1015vw*		
998w	*1015vw*		1003w		*1000vw*		*1001vw*
974w	*1002vw*	*1001vw*	980w	986w	*985vw*		*989vw*
921vw	*935vw*	*937vw*	*924vw*	*950vw*	*923vw*		*950vw*
	892vw	*915vw*	*892vw*				*918vw*
	881vw	*871vw*	860w	*879vw*	*862vw*		*864vw*
851w	860w	*824vw*	*815vw*				
		760vw	*768vw*		*804vw*		
			729vw				
	702w		694w	699m	700w		700m
677w					*679vw*		
					632vw		

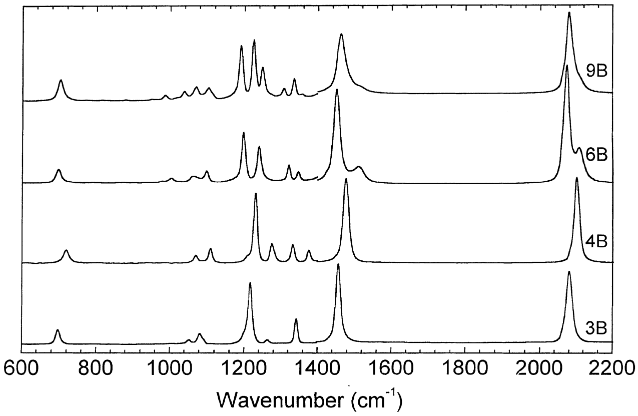

Fig. 4. FTIR-Raman spectra for samples of the nBCMU PDAs. From the top down: as-polymerised 9BCMU, as-polymerised 6BCMU, a single crystal of 4BCMU, and as-polymerised 3BCMU. Above 1400 cm^{-1}, the spectra are reduced in amplitude by factors of ca. 4 for 9BCMU and ca. 2 for the other three samples.

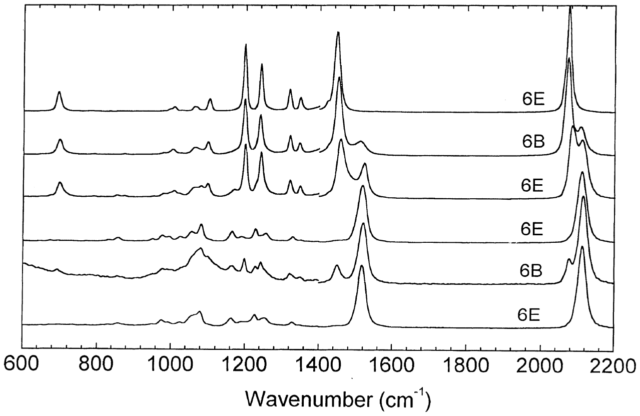

Fig. 5. FTIR-Raman spectra of as-polymerised and disordered samples of 6BCMU and 6ECMU. From the top down: as-polymerised 6ECMU, as-polymerised 6BCMU, 6ECMU film produced by slow evaporation, 6ECMU film produced by rapid evaporation, mechanically deformed 6BCMU and 6ECMU absorbed on filter paper. Above 1400 cm^{-1}, the spectra are reduced in amplitude by a factor ca. 2.

Table 2
FTIR-Raman frequencies for selected examples of the nB(E)CMU achiral polydiacetylenes; differences in frequency between as-polymerised samples of nBCMU and nECMU are small. Frequencies are in cm^{-1} with an accuracy of 2 cm^{-1}. Relative strength is indicated by: vs, very strong (bold); s, strong (underlined); m, medium; w,weak; sh, shoulder and very vw, very weak (italic)

3B^{a}	4B^{b}	6E^{a}	3B^{c}	9B^{c}	6E^{d}	6B^{e}
					2111vs	**2115vs**
2081vs	**2080vs**	**2073vs**	**2083vs**		**2075vs**	2077m^{f}
					1515vs	**1518vs**
1456vs	**1456vs**	**1446vs**	**1462vs**	**1454vs**		1450m^{f}
	1356w	1348m		*1358vw*		
1343m		1320m	1342m	1335m	1329w	*1321vw*
	1311m			1309w		
1263vw	1232m	1242s	*1261vw*	1250m	1250w	1241w
1216s	1211s		1217s	1225s	1228w	
	1190vw	1198s		1188s		1198w
					1163w	1162w
				1112s^{h}		
1081w	1088m	1101m	1082w	1105w		
		1062w		1072w	1080w	1072m
1052vw	1049w	*1028vw*	*1051vw*	1039w	1050s^{h}	
		1012w		*1014vw*		
		990vw		989w	976w	
	916vw			*949vw*		
		875vw		*877vw*		
				815vw		
		775vw		*772vw*		
698m	698m	694m	698m	696m		

[a] As-polymerised, solvent extracted samples.

[b] Single crystal.

[c] Films cast from chloroform solution.

[d] Polymer absorbed on filter paper (very weak lines are excluded because of possible contributions due to incomplete subtraction of the filter paper background).

[e] Mechanically deformed sample.

[f] Residual undeformed polymer.

1400 cm^{-1}. The spectra of 6BCMU and 6ECMU samples are typical (Fig. 5). For films of the chiral polymers obtained by slow evaporation, the –C=C– and –C≡C– stretching vibrations show considerable variation from sample to sample and less dramatic changes are observed below 1400 cm^{-1} than for the achiral polymers (Fig. 6). The spectra of samples formed by rapid evaporation are simpler, being similar to those of the achiral polymers (Fig. 6). Frequencies of the Raman bands for some typical disordered samples are listed in Table 1 for the chiral polymers and Table 2 for the achiral polymers.

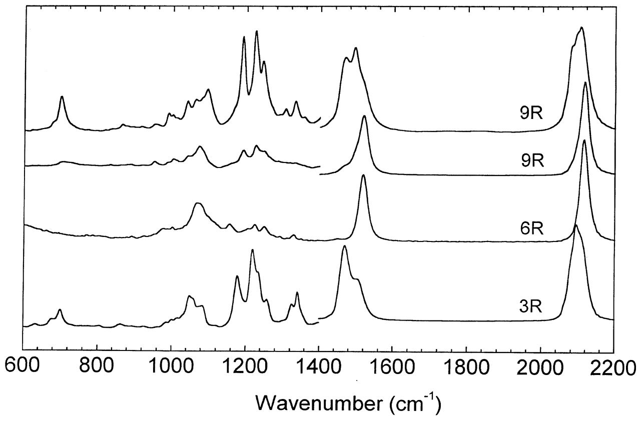

Fig. 6. FTIR-Raman spectra of solvent cast and filter paper absorbed samples of the chiral polymers. From the top down: 9RMBU film (slow evaporation), 9RMBU absorbed on filter paper, 6RMBU film (rapid evaporation) and 3RMBU film (slow evaporation). Above 1400 cm^{-1}, the spectra are reduced in amplitude by a factor ca. 2.

4. Discussion

The correlation between vibration frequency and chain length for the *n*-alkanes [39] has been shown to be of value in the interpretation of the spectra of more complex compounds [40]. For 3BCMU, the monomer crystal structure shows that the methylene group next to the diyne group is not trans to the other methylenes [28]. However, it has been argued, on the basis of the resonant-Raman spectrum and unit cell dimensions, that an all-trans sequence occurs in the polymer [34]. For 4BCMU, a trans sequence is indicated by the structural data [30,32,34]. Crystal structures have not been reported for either 6- or 9BCMU but it is known that both have two crystal modifications [34], as shown by the presence of two components for the –C=C– and –C≡C– stretching vibrations (Fig. 4). Modelling indicates that packing with all-trans alkyl chains is feasible for both polymers. Hence, features in the spectra of the nBCMU and nECMU polymers materials below 1400 cm^{-1} can be related to the vibrations of the *n*-alkanes. For the polymers with $n \geq 4$, the frequencies of the peaks observed between 1300 and 1400 cm^{-1} are in close agreement with those of the methylene wagging mode vibrations of the equivalent alkyl chains in the *n*-alkanes [39]. The more intense features between 1150 and 1300 cm^{-1} follow the same trends as the methylene twisting-rocking modes of the *n*-alkanes, but with an offset in frequency. These vibrations occur in the vicinity of the backbone mode at ca. 1200 cm^{-1} [1,7] and a shift in frequency due to interaction with this mode is possible. Below 1100 cm^{-1}, the correlation of the peaks observed for 9BCMU with the *n*-alkane methylene twisting-rocking modes is good. The correlation is reasonable for $n = 3$ and is poor for $n = 2$. However, 2BCMU polymerises to give cross-linked polymer and oligomers with a mean length of less than 100 repeat units [35,41] and, in addition, vibrations from the urethane moiety are likely to contribute to the spectrum. The observed correlation is consistent with the occurence of all-trans alkyl chains in the pendent groups of the nB(E)CMU polymers with $n \geq 3$.

Comparison of the spectra of the chiral and achiral polymer (Figs 2 and 4) shows that the former have more complex spectra than the latter, with the notable exception of the 9R(S)MBU and 9BCMU that have very similar spectra. The structure in the –C=C– and –C≡C– stretching vibration peaks of the chiral polymers indicates that the as-polymerised samples contain polymer chains with different microstructures. The fact that the structure seen in the spectra of samples with opposite chirality is in general identical (Fig. 4) shows that this reflects the inherent structure of the as-polymerised, solvent-extracted samples. Some of the different polymer modifications may result from relaxation of polymer micro-crystals during the extraction process. However, given the complex polymerisation behaviour of 3BCMU and 4BCMU [28–30] and the different crystal modifications found for 6BCMU and 9BCMU [34], it is probable that they derive from different crystalline phases that are either present in the monomer samples or produced during the polymerisation process. As-polymerised samples of the 3R(S)MBU PDAs show slight variability in the strength of the principal components of the broad –C=C– and –C≡C– vibration peaks. These polymers adopt several different ordered forms in solutions and films [23], indicating molecular conformations with small energy differences. This is also likely to occur for the monomer giving rise to varying proportions of different crystal modifications. The complex structure of the spectra of the chiral polymers in the region below 1400 cm^{-1} indicates that the alkyl chains in the pendent groups adopt a variety of structures rather than the all-trans structure found in the nB(E)CMU polymers. Thus, the different microstructures, indicated by the multiplicity of the peaks above 1400 cm^{-1}, have distinct conformations of the alkyl chains in the pendent groups. Such differences have been indentified as the origin of the different solid phases of nBCMU PDA crystals observed at elevated temperatures [33–35].

The spectra of samples obtained by casting films from solution, mechanically deforming the polymer, and by absorption on to filter paper are affected by the induced disorder. For 6B(E)CMU (Fig. 5) as-polymerised, solvent-extracted samples have a simple pattern of peaks below 1400 cm^{-1} and sharp peaks above 1400 cm^{-1}. Two components are observed in the latter peaks for 6BCMU indicating two crystal modifications [34], while 6ECMU has single peaks indicating a unique crystal structure. 6ECMU films obtained by slow evaporation of a chloroform solution, which have smooth surfaces with a green metallic lustre, have –C=C– and –C≡C– peaks with two components shifted up in frequency relative to those in the as-polymerised samples (Fig. 5). Below 1400 cm^{-1}, there are only small differences in relation to the as-polymerised sample. Thus, slow evaporation produces an ordered polymer with slightly less order than that present in the as-polymerised crystals. Rapid evaporation on either glass or filter paper gives red polymer with the –C=C– and –C≡C– stretching vibrations at ca. 1518 and 2115 cm^{-1} respectively; values similar to those reported for resonant-Raman spectra [34,35]. The mechanically deformed sample of 6BCMU contains traces of as-polymerised material; however, the principal high frequency peaks seen in the spectra (Fig. 5) are those of highly disordered material. The spectral features below 1400 cm^{-1} are weakened and broadened for all these disordered samples.

The introduction of disorder into the chiral polymers has similar effects. However, for films obtained by slow evaporation, the –C=C– and –C≡C– vibration frequencies vary noticably from polymer to polymer (Fig. 6). For 3R(S)MBU, there is a small reduction in frequency (Fig. 1). For 6RMBU the spectrum is simplified, with a single peak coinciding with the largest peak seen in the as-polymerised samples, and for 9RMBU there is a complicated peak structure with an increase in vibration frequency. Relative to the as-polymerised samples, there are only minor changes in peak strengths and frequencies below 1400 cm^{-1} for such films (cf. 3RMBU and 9RMBU, Figs 2 and 6). These changes are less marked than for equivalent samples of the achiral polymers and can be interpreted as the result of a redistribution of polymer chain conformations between structures either already present in the as-polymerised samples or closely related to them. The former appears to be true for 3R(S)MBU. Intensity changes of the overlapping peaks, seen in the as-polymerised samples, seem to be a likely cause of the apparent frequency shifts of the –C=C– and –C≡C– vibrations. For films and polymer absorbed on filter paper, where solvent evaporation was rapid, the structure in the low frequency region of the spectra is indistinct and the –C=C– and –C≡C– vibrations appear as single peaks at ca. 1518 and 2115 cm^{-1} respectively. The spectra are similar to those of achiral polymer samples prepared in

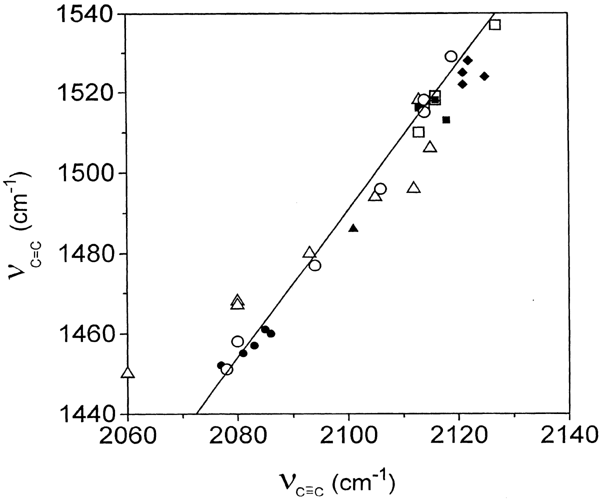

Fig. 7. Variation of the –C=C– and –C≡C– vibration frequencies for nBCMU samples, solid symbols from Ref. [35], and nR(S)MBU samples: ○, as-polymerised; △, films (slow evaporation), and; ●, rapidly evaporated and filter paper absorbed samples.

the same way (cf. mechanically deformed 6BCMU, Fig. 5, and 6RMBU film and 9RMBU on filter paper, Fig. 6). Hence strong perturbation of the pendent group structure has the same effect for both chiral and achiral PDAs.

The FTIR-Raman spectra (Figs 2 and 3,5 and 6) show that the structure of the pendent groups in the polymerised chiral polymers is not random since the features seen below 1400 cm^{-1} are clearer and stronger than those observed for disordered polymers. The similarity of the spectra for 9R(S)MBU and 9BCMU below 1400 cm^{-1} indicates that the pendent groups of 9R(S)MBU have predominantly trans alkyl chains. The –C=C– and –C≡C– vibrations of 9R(S)MBU as polymerised samples have less inherent structure than the other chiral polymers. Molecular models indicate that an all-trans $-(CH_2)_9-$ sequence allows hydrogen-bonds to be formed for both monomer and polymer. Furthermore, the FTIR-Raman spectrum of 9-2NA polymer [41] (Fig. 1) is similar to those of 9R(S)MBU and 9BCMU, indicating that the $-(CH_2)_9-$ chains allow efficient packing to be achieved even for very large terminal moieties. The FTIR-Raman spectra show that for the other chiral polymers the alkyl chains have more complex geometry. The bulky chiral moieties in the pendent groups are adjacent to the sites where hydrogen-bonds can be formed. It is likely that steric hindrance will result in competition between structures with and without hydrogen bonds. Molecular models show that if hydrogen bonds are formed the polymer backbone must be helical with a twist that decreases as *n* increases. The observed strength of the circular dichroism does not indicate the occurrence of such dependence on *n* [41]. The linear optical spectra of solutions and films of the chiral polymers also provide evidence for the presence of several polymer structures [31,41], lending further support to the interpretation of the FTIR-Raman data presented here.

2R(S)MBU appears to be an exception to these general observations since the spectra are relatively simple (Fig. 3). However, this is deceptive since there are more features below 1400 cm^{-1} than for 3BCMU (Fig. 4). These materials are probably cross-linked polymers and oligomers, as observed for 2BCMU [34,41]. Post-polymerisation extraction of monomer will then produce disordered chains, as indicated by the high frequencies of the –C=C– and –C≡C– vibrations for 2R(S)MBU (Fig. 3; Table 1).

These results also pose some general question that require further investigations. In the near-resonant regime, the backbone vibrations have been observed to have very broad asymmetric line shapes due to averaging over the distribution of polymer chain structures in solutions and disordered films [12,14]. The same should be true for the FTIR-Raman spectra since the scattering is dominated by the coupling of the backbone π-electrons and the backbone vibrations [20,21]. However, broad peaks are observed only when there are several distinct components present (Figs 2 and 3,5 and 6). The linewidths for the disordered samples appear similar to those of ordered samples (Figs 2 and 4,5 and 6). The measured full widths at half height of the –C=C– and –C≡C– peaks for a single crystal of pTS (Fig. 1), the 4BCMU single crystal, and as-polymerised, rapidly precipitated and mechanically deformed 6BCMU samples are 15, 17, 19, 27 and 26 ± 2 cm^{-1}, respectively. There is no discernible asymmetry in any of these Raman bands. The much larger value for 4BCMU films reported by Zheng et al. [14] appears to result from the overlapping of three distinct bands with structure very similar to that observed for films of related polymers (Figs 5 and 6). For nS(R)MBU, nB(E)CMU, 9-2NA, etc., PDAs with strong static disorder, the –C=C– and –C≡C– peak frequencies and widths are 1518, 2115 and 26 ± 3 cm^{-1}, independent of the structure of the pendent group, see also ref. [35]. This suggests a moderate distribution of backbone structures about a common mean determined principally by the conjugated chain rather than being imposed on it by the packing of the pendent groups.

The frequencies of the –C=C– and –C≡C– vibrations shift in response to changes in bond length caused by external forces [7–10], changes in crystal structure in partially and fully polymerised samples [2–6] and loss of crystal structure [11–15,35]. The shifts produced by mechanical deformation of crystals differ from those produced by the disorder induced in nBCMU polymers by heating and melting [35]. The latter have been associated with deviations of the conjugated backbone from planarity [35]. Comparison of the data for the different nR(S)MBUs samples with that reported for the nBCMUs (Fig. 7) shows a similar relationship between the –C=C– and –C≡C– vibration frequencies; the slope of a fit to the nBCMU data is 1.71 ± 0.08 [35], while that for as polymerised nR(S)MBU samples is 1.83 ± 0.09. Thus, while one can conclude that the response of these polymers to structural changes in the pendent groups follows a generic behaviour, there is currently no adequate microscopic model with which to interpret the collected data (Fig. 7). Furthermore, although the close similarity of the Raman spectra of the most disordered samples, noted above, implies similar backbone structures for nB(E)CMU and nR(S)MBU polymers, the CD spectra [22] indicate that the latter have helical backbones. This contradicts the conclusion, reached in the previous paragraphs, that the pendent groups do not influence the conjugated backbone. Hence, there is a clear need for more detailed microscopic molecular modelling, which includes the effects of static and dynamic disorder, of these and other PDAs.

5. Conclusions

The FTIR-Raman spectra of the chiral nR(S)MBU PDAs show that as-polymerised samples, from which residual monomer has been removed by solvent extraction, contain polymer chains with different, distinct micro-morphologies. Comparison with the spectra of as-polymerised samples of the achiral nB(E)CMU polymers indicates that, in general, the alkyl chains in the pendent groups of the chiral polymers are not in an all-trans conformation. However, the spectra of disordered samples of both chiral and achiral polymers show that the pendent groups in the as-polymerised samples of the chiral polymers are not completely randomised. Thus, the pendent groups must contain alkyl chains with distinct structures, e.g. with gauche conformers at particular positions.

The 9R(S)MBU polymers are an exception; the spectra of these polymers and a variety of other PDAs with $-(CH_2)_9-$ chains in the pendent groups indicate that an all-trans structure occurs independent of the terminal moiety. Molecular modelling supports the conclusion that a single conformation is more probable for the materials with longer alkyl chains in the pendent groups. For short alkyl chains, the bulky chiral moiety present in the nR(S)MBU polymers will hinder close packing of the pendent groups and the formation of hydrogen bonds between them. Hence, there is likely to be competition between structures with alkyl chain conformations that permit hydrogen bonds to form and those that inhibit hydrogen-bonding between the pendent groups. The result will be monomer and polymer samples with more than one crystal modification, as observed in the FTIR-Raman spectra.

Acknowledgements

Thanks are due to the Alexander von Humboldt Foundation for a fellowship, to Prof. M. Schwoerer, Experimentalphysik II, Universität Bayreuth for access to research facilities, to T. Fehn for the spectrum of the 4BCMU single crystal and assistance in performing the experiments, to D.J. Ando for the PDA samples and the University of Durham for granting research leave.

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