Synthesis and infra-red spectroscopic characterization of random copolymers of 4-vinylphenol with n-alkyl methacrylates

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A series of random copolymers of 4-vinylphenol with n-alkyl methacrylates were synthesized by free-radical copolymerization of 4-t-butyldimethylsilyloxystyrene and the corresponding alkyl methacrylates, followed by selective removal of the t-butyldimethylsilyl protective group. Copolymerizations were performed in benzene at 60°C using azobisisobutyronitrile as an initiator and reactivity ratios were determined using the Kelen–Tüdös method. Removal of the protective group was effected by tetrabutylammonium fluoride in tetrahydrofuran at ambient temperature. An infra-red spectroscopic characterization of these copolymers is reported.

(Keywords: random copolymers; 4-vinylphenol; n-alkyl methacrylates; synthesis; infra-red spectroscopy)

INTRODUCTION

Much of our previously published work on theoretical and experimental studies of the phase behaviour of polymer blends pertains to systems involving two (co)polymers, the first of which self-associates through intermolecular hydrogen bonding, such as a polyamide, a polyurethane, poly(4-vinylphenol) (PVPh), styrene-*co*-4-vinylphenol (STVPh), poly(hexafluoroisopropanol styrene) (PHFPS), etc., and the second of which does not self-associate to any measurable extent, but is capable of forming a hydrogen bond (inter-association) with the first, such as the poly(n-alkyl methacrylates) (PAMA), poly(vinyl acetate) (PVAc), ethylene-*co*-vinyl acetate (EVA), poly(ethylene oxide) (PEO), styrene-*co*-vinylpyridine, etc.[1,2]. In all these cases each of the (co)polymers in the blends may be described in terms of a *specific repeat unit* that contains a *single* site capable of forming a specific interaction. Employing a lattice model developed in our laboratories we have been remarkably successful in predicting miscibility windows and maps for such systems by assuming that the *non*-specific interacting monomer, e.g. ethylene or styrene, acts principally as a 'diluent'[1,3].

Recently we have begun to explore more complicated systems involving multiple specific interaction sites. These include ternary blend systems[4], for example, PVPh–PEO–PVAc (or PMMA), an unusual system where each binary pair is miscible, and binary blends containing the poly(hydroxy ether of bisphenol A) (Phenoxy)[5], a homopolymer that contains both a hydroxyl group and two ether oxygens within its specific repeat unit. We commonly confront copolymers, however, that are composed of more than one comonomer and contain *different* sites capable of specific interactions through hydrogen bonding. Good examples include random copolymers of alkyl methacrylates with 4-vinylphenol (AMAVPh). Unlike the styrene-*co*-vinylphenol (STVPh) copolymers, where self-association may be described by two equilibrium constants (i.e. the formation of hydroxyl–hydroxyl dimer and chain-like multimers) and the styrene comonomer is considered just a 'diluent', the AMAVPh copolymers have two sites capable of specific interactions and an additional equilibrium constant is necessary to describe the competing formation of hydroxyl–ester hydrogen bonds for this copolymer in the pure state. Thus by introducing a monomer containing a competing hydrogen bonding site into VPh copolymers we have simultaneously 'diluted' pure PVPh and changed the nature of self-association *vis-à-vis* STVPh. The ability to handle systems composed of (co)polymers containing multiple specific interaction sites, both theoretically and experimentally, is important because the interplay of self- and inter-association plays a crucial role in the phase behaviour of polymer blends[1,2,4]. It is for this reason, and the fact that copolymers containing carbonyl and hydroxyl groups are particularly amenable to infra-red spectroscopic analysis, that we embarked on a programme to synthesize essentially random AMAVPh copolymers.

It is well known that solution free-radical polymerization of 4-vinylphenol generally produces ill-defined, highly coloured, low-molecular-weight PVPh, caused primarily by chain transfer and other side reactions (e.g. oxidation) to the phenolic hydroxyl group during the course of polymerization. Several methods have been developed to prepare high-molecular-weight PVPh, the general strategy being to polymerize 4-vinylphenol with the phenolic hydroxyl group protected, and then subsequently

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transforming the resulting polymer to PVPh following deprotection. A number of protective groups have been employed for this purpose, and the notable ones include t-butoxycarbonyl[6], trialkylsilyl[3,7,8] and acetyl[9-11] groups. The latter has been widely used in the preparation of PVPh and styrene–vinylphenol copolymers[9,10].

The acetyl protective group is not appropriate for the synthesis of random AMAVPh copolymers, however, since complete removal of the acetyl group from the parent poly(4-acetoxystyrene) requires strong chemical reagents (e.g. hydrazine), which also react with the ester group of the methacrylate (yielding undesirable methacrylic acid groups). Accordingly, we require a protective group that can be selectively removed from the parent AMAVPh copolymers without hydrolysing the ester groups. An ideal candidate for this purpose appears to be t-butyldimethylsilyl (TBDMS), which has been employed in the synthesis of PVPh by anionic polymerization[7,8]. We have previously used this protective group in the synthesis of random STVPh copolymers by solution free-radical polymerization[3]. The important point is that the TBDMS protective group can be removed from the parent molecule under mild and neutral reaction conditions with tetrabutylammonium fluoride, which reacts selectively with the silyl group in tetrahydrofuran (THF) at room temperature.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF), tetrahydrofuran (THF), benzene, 4-hydroxybenzaldehyde, t-butyldimethylsilyl chloride, methyltriphenylphosphonium bromide, tetrabutylammonium fluoride, azobisisobutyronitrile (AIBN) and styrene were purchased from Aldrich Chemical Co. Inc. Styrene was passed through a short column of neutral alumina and distilled from calcium hydride prior to use. AIBN was recrystallized from acetone. DMF and THF were distilled, respectively, from magnesium sulfate and sodium/benzophenone immediately before use. Other reagents were used without further purification. All glassware was flame-dried prior to use.

Preparation of 4-(t-butyldimethylsilyloxy)benzaldehyde

To a solution of 4-hydroxybenzaldehyde (26.2 g, 0.21 mol) and t-butyldimethylsilyl chloride (38.7 g, 0.26 mol) in dry DMF (150 ml) was added imidazole (35.2 g, 0.51 mol). The mixture was stirred overnight at ambient temperature and then poured into ice–water. The organic layer was extracted with diethyl ether and washed, successively, with H_2O, 5% $NaHCO_3$ aqueous solution and H_2O, and dried with magnesium sulfate. Evaporation of the solvent gave 46 g (92%) of the crude material. Vacuum distillation afforded 43 g of the pure 4-(t-butyldimethylsilyloxy)benzaldehyde. ^1H n.m.r. (360 MHz, $CDCl_3$): δ (ppm) = 0.21 (s, 6H, Si–CH_3); 0.97 (s, 9H, Si–C–CH_3); 6.96 (d, 2H, aryl-H, $J = 8.4$ Hz); 7.82 (d, 2H, aryl-H, $J = 8.7$ Hz); 9.88 (s, 1H, CHO).

Preparation of p-*(t-butyldimethylsilyloxy)styrene (t-BSOS)*

A suspension of 66.8 g (0.19 mol) of methyltriphenylphosphonium bromide in 270 ml of dry THF was treated with 74.8 ml of 2.5 M n-butyllithium (0.19 mol) under a nitrogen atmosphere. After stirring for 30 min at room temperature, the red solution was treated with a solution of 40.0 g (0.17 mol) of 4-(t-butyldimethylsilyloxy)benzaldehyde in 50 ml of dry THF. The solution was stirred overnight at ambient temperature. The mixture was poured into ice–water and extracted with diethyl ether. The organic layer was washed with water, dried over magnesium sulfate and concentrated. The crude product was purified by distillation under vacuum (75–78°C/0.1 mmHg) to give 34 g of the pure monomer. ^1H n.m.r. (360 MHz, $CDCl_3$): δ (ppm) = 0.21 (s, 6H, Si–CH_3); 0.97 (s, 9H, Si–C–CH_3); 5.10 (d, 1H, =CH_2, *cis*, $J = 9.9$ Hz); 5.57 (d, 1H, =CH_2, *trans*, $J = 10.6$ Hz); 6.60 (dd, 1H, =CH, $J = 9.9$ and 10.6 Hz); 6.78 (d, 2H, aryl-H, $J = 8.6$ Hz); 7.26 (d, 2H, aryl-H, $J = 11.9$ Hz).

*Preparation of n-alkyl methacrylate-*co*-t-BSOS copolymers*

Solution copolymerization of ethyl, n-butyl and n-decyl methacrylates with t-butyldimethylsilyloxystyrene in benzene was performed in glass reaction flasks containing condensers at 60°C under a nitrogen atmosphere. AIBN was employed as an initiator and the mixture was stirred for about 6 h. Samples of the copolymers used to determine reactivity ratios were taken from the reaction flasks in the early stage of copolymerization when the degree of conversion was low (between 4 and 9%). The copolymerization was terminated by the addition of methanol and the copolymer was purified by repeatedly dissolving in THF and precipitating in methanol.

*Desilylation: preparation of n-alkyl methacrylate-*co*-vinylphenol copolymers*

To a solution of the n-alkyl methacrylate-*co*-t-BSOS copolymer (3.0 g) in THF (60 ml) and acetic acid (5 ml) was added tetrabutylammonium fluoride (2 mol per t-butyldimethylsilyl group). The addition of a small amount of acetic acid was found necessary to ensure that the reaction mixture remained in a homogeneous state until completion of the desilylation. The mixture was stirred at ambient temperature for approximately 2 h. Following removal of the majority of the solvent, the viscous solution was poured into water and stirred for ca. 10 min. The copolymer was then collected and redissolved in THF. This solution was added dropwise into a large excess of water. Repeating this procedure several times yielded the pure, white poly(n-alkyl methacrylate-*co*-4-vinylphenol).

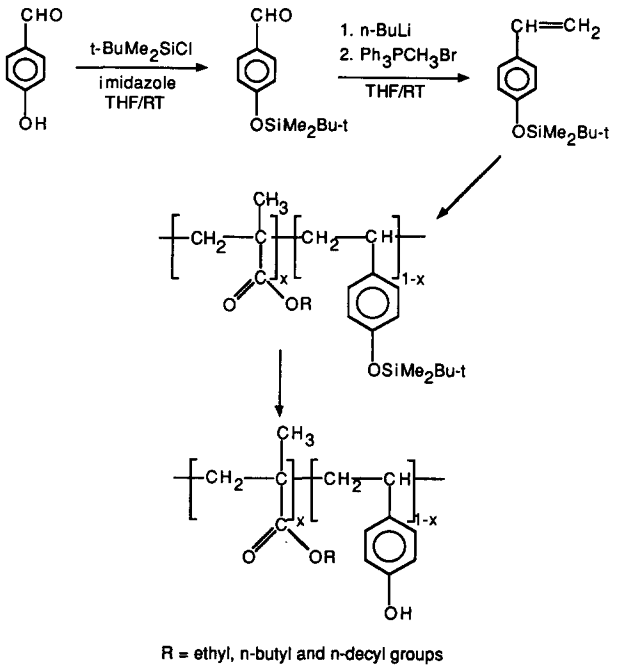
Spectroscopic characterization

^1H and ^{13}C n.m.r. spectra were obtained on Bruker WP-200 and WM-360 *FT*n.m.r. spectrometers. Deuterated chloroform and deuterated acetone were used as solvents for the n-alkyl methacrylate copolymers with t-BSOS and VPh, respectively. Infra-red spectra were recorded on a Digilab model FTS-60 Fourier transform infra-red (*FT*i.r.) spectrometer using a minimum of 64 co-added scans at a resolution of 2 cm^{-1}. Spectra recorded at elevated temperatures were obtained using a heating cell mounted inside the sample chamber. Temperature was regulated by a Micristar 828D digital process controller, which has a reported accuracy of ±0.1°C. Thin films of the copolymers were cast from THF solution onto potassium bromide windows at room temperature. All films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed[12]. Thermal analysis was conducted on a Perkin–Elmer differential scanning calorimeter (DSC-7) coupled to a computerized data station. A heating rate of 20°C $\min^{-1}$ was used in all experiments and the glass transition temperature was taken as the midpoint of the heat capacity change. Thermal gravimetric analyses were performed on a Perkin–Elmer TGS-2 at a heating rate of 10°C $\min^{-1}$. Molecular weights and molecular-weight distributions, based upon polystyrene standards, were determined by gel permeation chromatography (g.p.c.) using a Waters 150C GPC/ALC equipped with a refractive index detector and four μStyragel columns (100 000, 10 000, 500 and 100), connected in series.

RESULTS AND DISCUSSION

Scheme 1 summarizes the general approach used to synthesize n-alkyl methacrylate-*co*-vinylphenol copolymers (AMAVPh). In essence, there are three steps: (1) preparation of the protected t-BSOS monomer; (2) copolymerization of t-BSOS with the respective alkyl methacrylates; and (3) deprotection of the phenolic hydroxyl groups. Specifically, we initially synthesized three sets of the hydroxyl-protected copolymers of varying composition, i.e. poly(n-decyl methacrylate-*co*-t-butyldimethylsilyloxystyrene) (DMAtBSOS), poly(n-butyl methacrylate-*co*-t-butyldimethylsilyloxystyrene) (BMAtBSOS) and poly(ethyl methacrylate-*co*-t-butyldimethylsilyloxystyrene) (EMAtBSOS). These copolymers were obtained in 50–70% yield and their chemical compositions were determined by ^{1}H n.m.r. spectroscopy. *Figure 1* shows a typical ^{1}H n.m.r. spectrum of a DMAtBSOS copolymer containing 43 mol% t-BSOS (denoted DMAtBSOS{43}). The aromatic protons of the phenol ring and the methylene group that is immediately next to the oxygen of the ester side chain (i.e. the $-OCH_2-$) were employed as a quantitative analytical probe. The broad peaks occurring between 3.2 and 4.2 ppm in the spectrum represent different methylenes adjacent to ester oxygens that are differentiated in chemical shift by their spatial position relative to the phenol rings and their sequential distribution[13].

Table 1 lists the monomer feed and copolymer compositions from which reactivity ratios were calculated using the methodology of Kelen and Tüdös[14,15]. The results are displayed graphically for the DMAtBSOS



R = ethyl, n-butyl and n-decyl groups

Scheme 1

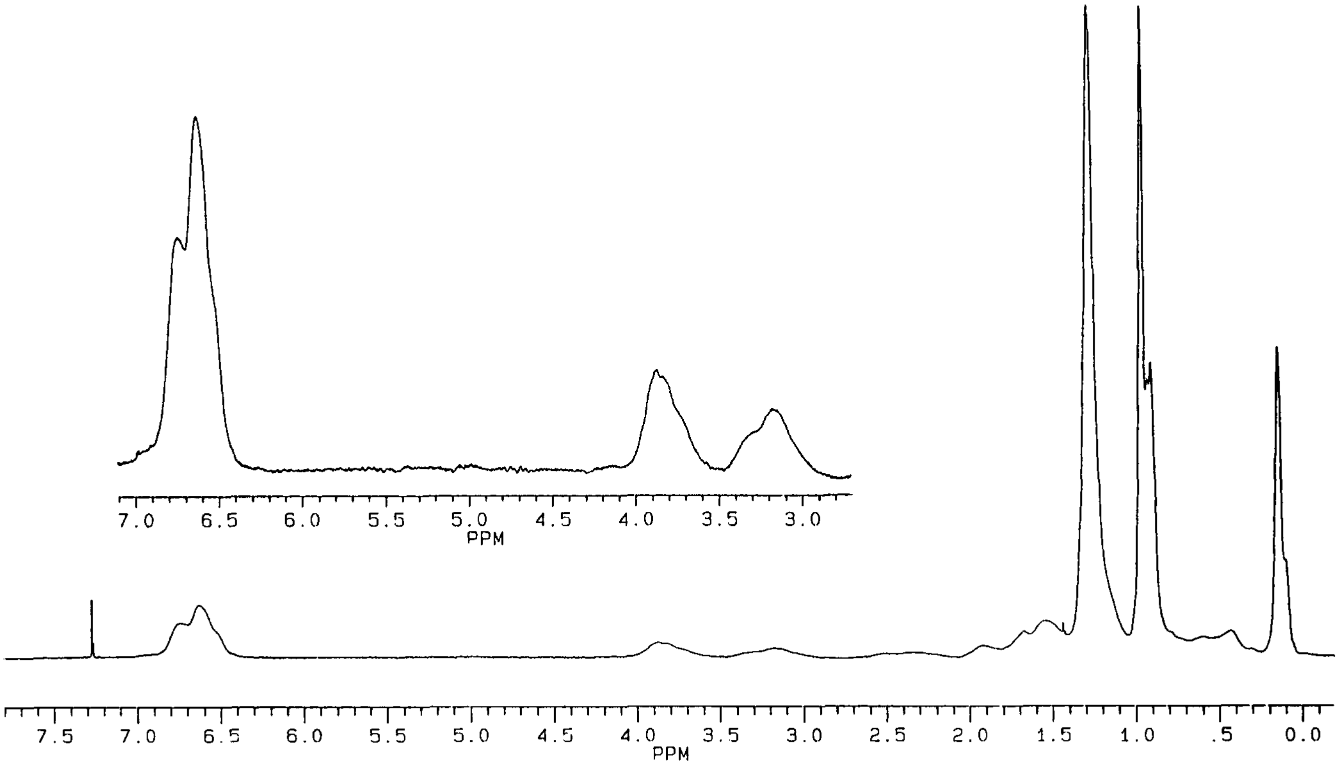


Figure 1 ^{1}H n.m.r. spectrum of DMAtBSOS copolymer containing 43 mol% t-BSOS

Table 1 Copolymer compositional and molecular-weight data[a]

Polymer	Monomer feed (mol%)		Polymer composition (mol%)		Number-average molecular weight[c]
	MA[b]	tBSOS[b]	MA	tBSOS	
DMAtBSOS{20}[d]	90	10	80.1	19.9	15 300
DMAtBSOS{32}	80	20	68.0	32.0	20 500
DMAtBSOS{42}	70	30	58.0	42.0	14 900
DMAtBSOS{50}	60	40	50.2	49.8	12 400
DMAtBSOS{52}	50	50	47.6	52.4	13 100
DMAtBSOS{66}	30	70	34.0	66.0	11 500
DMAtBSOS{77}	20	80	23.0	77.0	9900
DMAtBSOS{89}	10	90	11.0	89.0	10 500
BMAtBSOS{20}[e]	90	10	79.8	20.2	15 300
BMAtBSOS{39}	70	30	61.5	38.5	16 000
BMAtBSOS{50}	50	50	49.9	50.1	11 000
BMAtBSOS{52}	50	50	48.1	51.9	9000
BMAtBSOS{58}	30	70	41.9	58.1	13 900
BMAtBSOS{73}	20	80	21.2	72.8	15 100
EMAtBSOS{31}[f]	80	20	69.6	30.6	16 500
EMAtBSOS{53}	50	50	46.6	53.4	12 500
EMAtBSOS{65}	35	65	34.7	65.3	10 000

[a] Polymerization conditions: initiator = AIBN; solvent = benzene; temperature = 60°C
[b] MA = the respective methacrylates; tBSOS = t-butyldimethylsilyloxystyrene
[c] Determined by g.p.c. using polystyrene standards
[d] DMAtBSOS = poly(n-decyl methacrylate-*co*-t-butyldimethylsilyloxystyrene)
[e] BMAtBSOS = poly(n-butyl methacrylate-*co*-t-butyldimethylsilyloxystyrene)
[f] EMAtBSOS = poly(n-ethyl methacrylate-*co*-t-butyldimethylsilyloxystyrene)

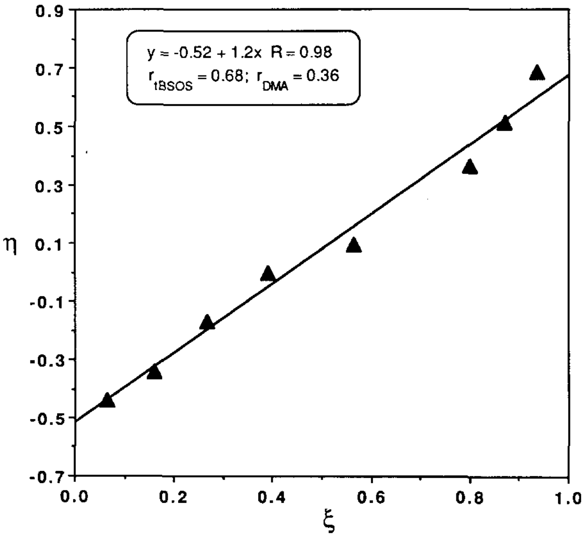


Figure 2 Kelen–Tüdös plot for the DMAtBSOS copolymers

copolymers in *Figure 2* from which values of $r_{tBSOS} = 0.68$ and $r_{DMA} = 0.36$ are calculated. The apparent linear relationship suggests that copolymerization of the two comonomers follows the simple two-parameter (terminal) model. Similar values of $r_{tBSOS} = 0.51$, $r_{BMA} = 0.36$ and $r_{tBSOS} = 0.68$, $r_{EMA} = 0.31$ are calculated for the BMAtBSOS and EMAtBSOS copolymers, respectively. The product of the reactivity ratios is in the range of 0.18–0.25, which indicates that the monomers are introduced into the polymer chain in an essentially random fashion with a slight tendency towards alternation. Also included in *Table 1* are the approximate number-average molecular weights of the t-BSOS copolymers determined by g.p.c. and based upon polystyrene standards. The copolymers produced are of relatively low molecular weight ($\approx$10 000–20 000) and have polydispersities close to 2. Because of the difficulties (adsorption, etc.) of performing accurate size exclusion chromatographic analysis of polymers that strongly hydrogen bond, such as the AMAVPh copolymers, we have assumed that the tBSOS precursor and ensuing VPh copolymer have the same degree of polymerization.

The desilylation procedure employed to produce the AMAVPh copolymers is an important step. Tetrabutylammonium fluoride in THF/acetic acid at ambient temperature is used to remove the t-butyldimethylsilyl protective group. As mentioned previously, t-butyldimethylsilyl was deliberately chosen as a protective group in this work because it was expected to be selectively and readily removed from the parent copolymers without causing hydrolysis of the methacrylate ester groups. Of particular concern was the possibility of a side reaction involving the substitution of the phenoxide for the alkoxide of the methacrylate. To ensure that tetrabutylammonium fluoride does not cause such a reaction, a poly(t-butyldimethylsilyloxystyrene) homopolymer was synthesized and subsequently treated with ethyl acetate under the same conditions as the copolymers. The *FT*i.r. spectrum of the resulting polymer (i.e. PVPh) showed no carbonyl stretching vibration band in the region of 1650 and 1800 cm^{-1}, indicating that reaction between the phenoxide and ethyl acetate did not occur during the course of desilylation.

The complete elimination of the protective groups and the regeneration of the phenolic hydroxyl groups were demonstrated by n.m.r. and *FT*i.r. spectroscopies.

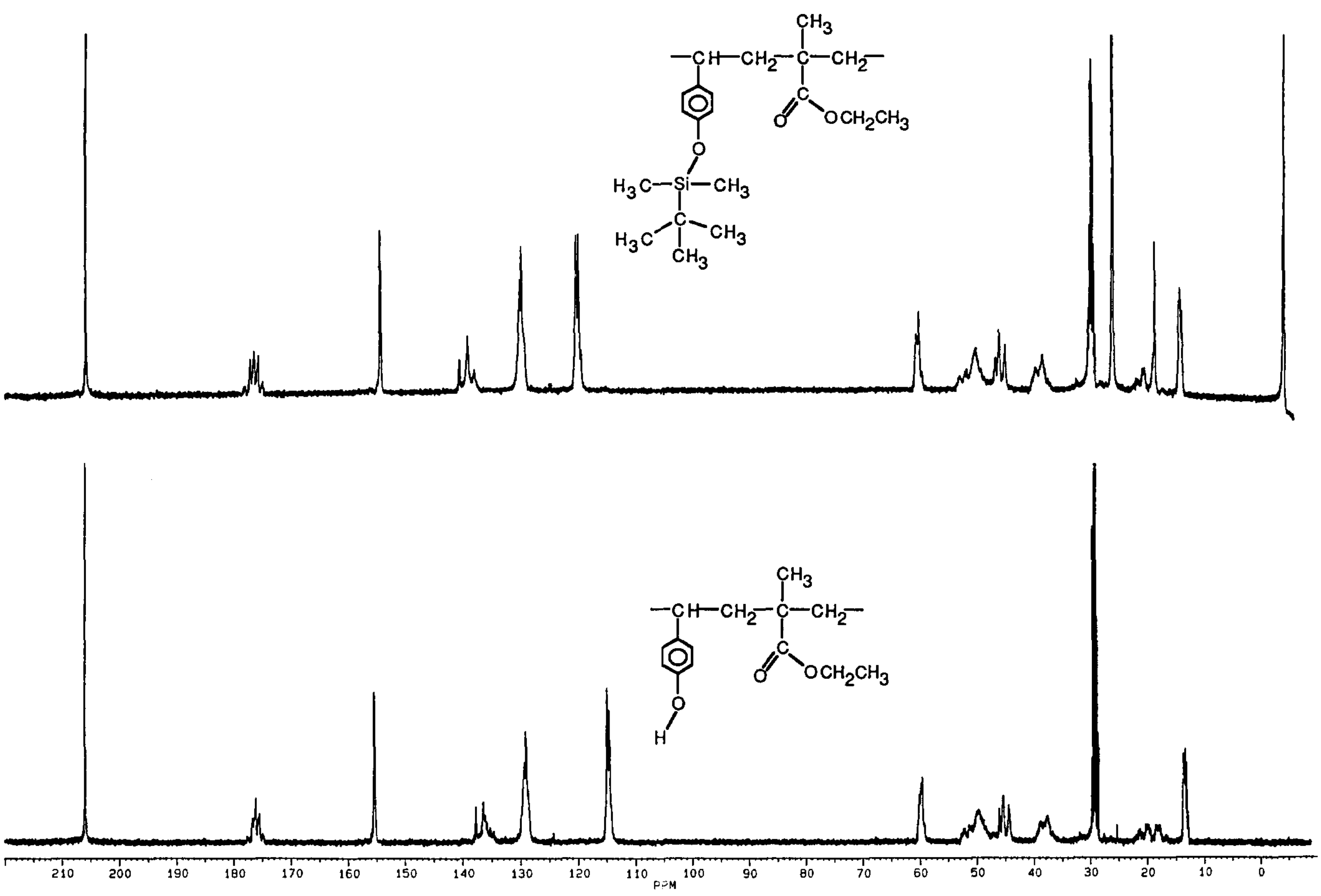


Figure 3 ^{13}C n.m.r. spectra of the EMA copolymer containing 52 mol% ethyl methacrylate before (top) and after (bottom) deprotection

Figure 3 shows typical ^{13}C n.mr. spectra of the EMA copolymers containing 52 mol% of ethyl methacrylate before (top) and after (bottom) deprotection. The absence of the n.m.r. peaks at around 0 ppm (the two methyl carbons attached to silicon), 19 ppm (the tertiary carbon of the t-butyl group) and 26 ppm (the three methyl carbons on the t-butyl group) after desilylation clearly indicates the absence of any t-butyldimethylsilyl residual. Corresponding ^{1}H n.m.r. spectra showed that the two peaks located at $\delta = 0.2$ and 0.9 ppm (see *Figure 1*) disappeared following desilylation. *Figure 4* compares the *FT*i.r. spectra of the DMA copolymers containing 57 mol% of n-decyl methacrylate before (A) and after (B) desilylation. Three major changes are observed: (1) the infra-red band seen at about 952 cm^{-1}, which is assigned to the Si–O stretching modes (spectrum A), is completely absent following desilylation (spectrum B); (2) a broad absorbance occurring between 3100 and 3700 cm^{-1} appears, indicating the presence of a distribution of hydrogen-bonded hydroxyl groups; and (3) spectrum A is characterized by a strong absorbance located at 1727 cm^{-1} attributed to the 'free' (non-hydrogen-bonded) carbonyl stretching vibration. An additional band centred at 1701 cm^{-1} is observed in spectrum B, which is assigned to the stretching mode of carbonyl groups that are hydrogen bonded to phenolic hydroxyl groups.

Further infra-red characterization of the AMAVPh copolymers as a function of composition and temperature is warranted, since we intend to use these materials in studies of the phase behaviour of polymer blends. We will first consider the carbonyl stretching region. *Figure 5* shows scale-expanded room-temperature infra-red spectra recorded in the region from 1650 to 1800 cm^{-1} for eight DMAVPh copolymers. Infra-red spectra obtained for the various EMAVPh and BMAVPh copolymers are very similar and are not shown. The interpretation of these spectra is akin to that of *miscible* poly(4-vinylphenol) blends with carbonyl-containing polymers such as polymethacrylates[1]. The relative intensities of the 'free' and hydrogen-bonded carbonyl bands centred at 1727 and 1701 cm^{-1}, respectively, vary systematically in favour of the latter as the VPh content in the DMAVPh copolymer increases. This simply reflects the stoichiometry of hydrogen bonding. Note also that from quantitative measurements of the fraction of hydrogen-bonded carbonyl groups we can calculate an equilibrium constant describing the inter-association of carbonyl groups that are hydrogen bonded to VPh hydroxyl groups[1]. *Figure 6* shows scale-expanded infra-red spectra of a DMAVPh copolymer containing 56 mol% VPh recorded as a function of temperature. As anticipated, the intensity of the 'free' band (1727 cm^{-1}) increases with increasing temperature at the expense of the hydrogen-bonded band (1701 cm^{-1}). Upon cooling from 220°C to room temperature, the changes are reversed and the spectrum recovers its original shape. This reflects the temperature dependence of the equilibrium constants describing the formation of hydrogen bonds, from which we can calculate the enthalpy of hydrogen bonding formation[1].

It is of interest to note that blends of the homopolymers PVPh and poly(n-decyl methacylate) (PDMA) are

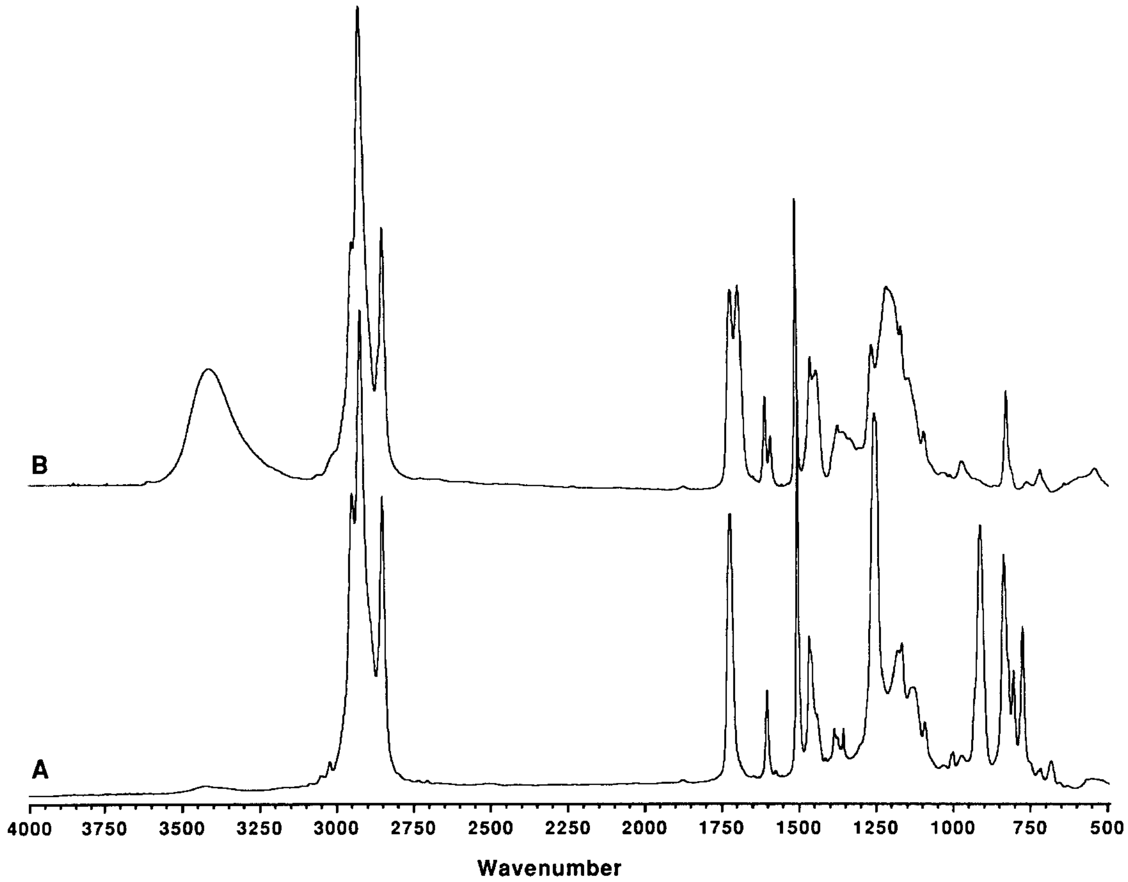


Figure 4 *FT*i.r. spectra of the DMA copolymer containing 43 mol% n-decyl methacrylate before (A) and after (B) deprotection

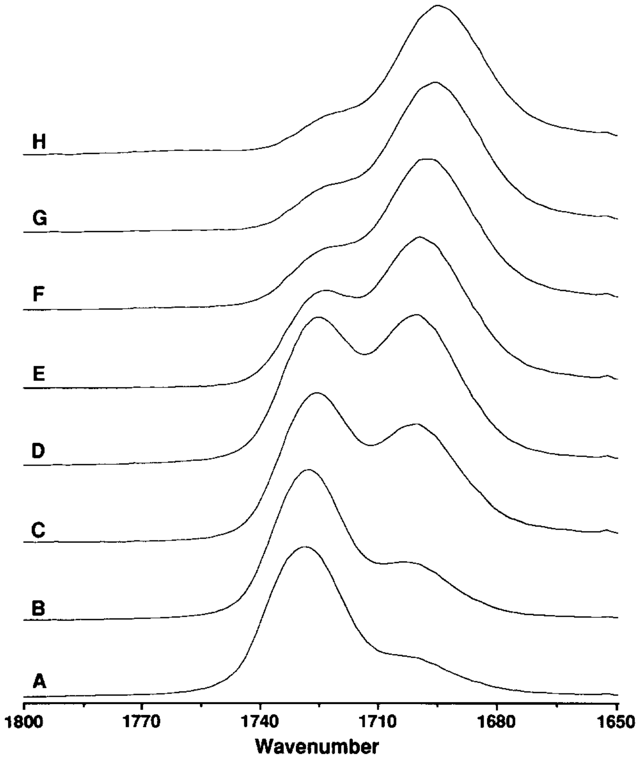


Figure 5 Scale-expanded *FT*i.r. spectra recorded at room temperature in the carbonyl stretching region for DMAVPh copolymers containing (A) 14, (B) 22, (C) 40, (D) 43, (E) 56, (F) 77, (G) 85 and (H) 93 mol% VPh

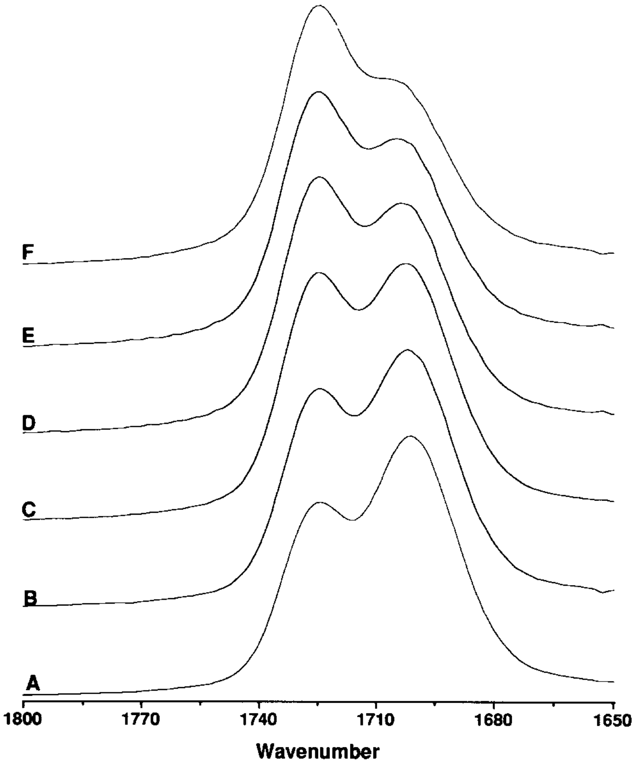


Figure 6 Scale-expanded *FT*i.r. spectra recorded as a function of temperature in the carbonyl stretching region for DMAVPh copolymer containing 56 mol% VPh at (A) 90, (B) 120, (C) 150, (D) 180, (E) 200 and (F) 220°C

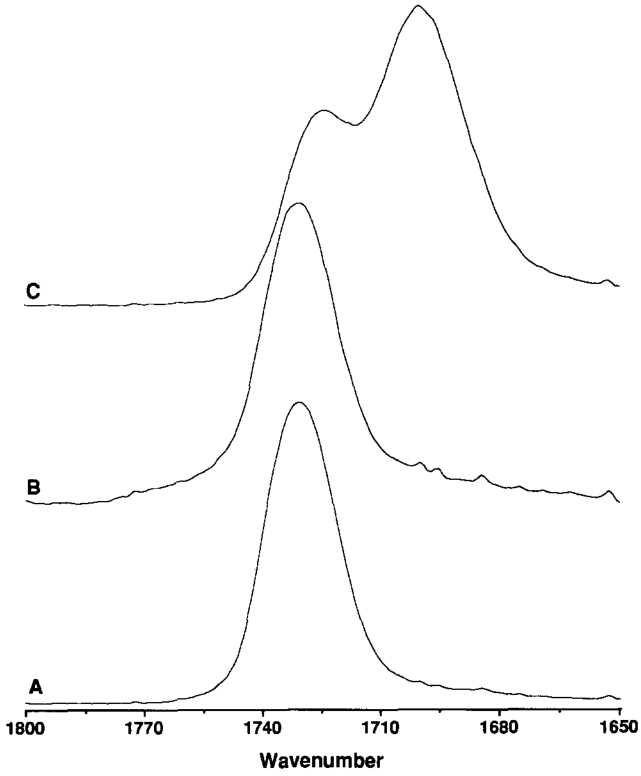


Figure 7 Scale-expanded *FT*i.r. spectra recorded at room temperature in the carbonyl stretching region for (A) PDMA, (B) a PDMA:PVPh = 44:56 (mole) blend and (C) a DMAVPh copolymer containing 56 mol% VPh

theoretically predicted to be immiscible over the entire temperature range[16]. Experimentally, films prepared of PVPh and PDMA are grossly phase separated and this is confirmed by infra-red spectroscopic studies, which corroborate that there are no detectable hydrogen bonding interactions between the phenolic hydroxyl groups and the carbonyl groups of PDMA. This is illustrated in *Figure 7*, which compares room-temperature infra-red spectra in the carbonyl stretching region of a 56:44 PVPh:PDMA blend (by mole) and the analogous DMAVPh copolymer containing approximately the same concentration of VPh. In the case of the copolymer, the DMA and VPh segments are forced together by being covalently attached in the copolymer chain and the system inevitably exists in a single phase (assuming little or no compositional variation of the DMAVPh copolymer). Accordingly, hydrogen-bonded carbonyl groups can now form owing to the close proximity of the VPh hydroxyl groups, which exist in the same phase. This is also consistent with the single glass transition temperatures observed for these copolymers, which vary systematically with copolymer composition[17].

Compared to the carbonyl stretching region of the infra-red spectrum, the interpretation of the hydroxyl stretching region of the AMAVPh copolymers is considerably more complicated and not readily amenable to quantitative analysis[1]. *Figure 8* shows scale-expanded room-temperature infra-red spectra recorded in the region from 3100 to 3700 cm^{-1} for the eight DMAVPh copolymers. Similar features are observed in the spectra of the various EMAVPh and BMAVPh copolymers. The spectrum of pure PVPh is shown in curve I in *Figure 8* and is characterized by a very broad band centred at 3360 cm^{-1}, which reflects the non-equilibrium* distribution of VPh hydroxyl groups that are hydrogen bonded to other hydroxyl groups in dimers and chain-like 'multimers'[1]. A second narrower band, observed at 3540 cm^{-1} as a shoulder on the high-frequency side of the broad hydrogen-bonded band, has been assigned to 'free' (non-hydrogen-bonded) hydroxyl groups. Note that we have consistently and intentionally placed the word *free* between quotation marks to signify that the hydroxyl groups exist in a specific environment and are not isolated in a totally inert matrix. This is important for the interpretation of the infra-red spectra of DMAVPh copolymers because, as we will see below, the frequency of the band attributed to 'free' hydroxyl groups depends upon whether the isolated hydroxyl group is primarily surrounded by aromatic or aliphatic moieties. In the case of PVPh (or STVPh copolymers, for that matter) isolated hydroxyl groups are in close proximity to a sea of aromatic rings and O–H···π interactions shift the frequency of the 'free' OH band to a lower value *vis-à-vis* isolated hydroxyl groups in a truly inert environment[18].

Spectra A through H in *Figure 8* show *scale-expanded* infra-red spectra of eight DMAVPh copolymers in the hydroxyl stretching region as a function of decreasing concentration of VPh. The broad hydrogen-bonded band narrows with increasing DMA and its

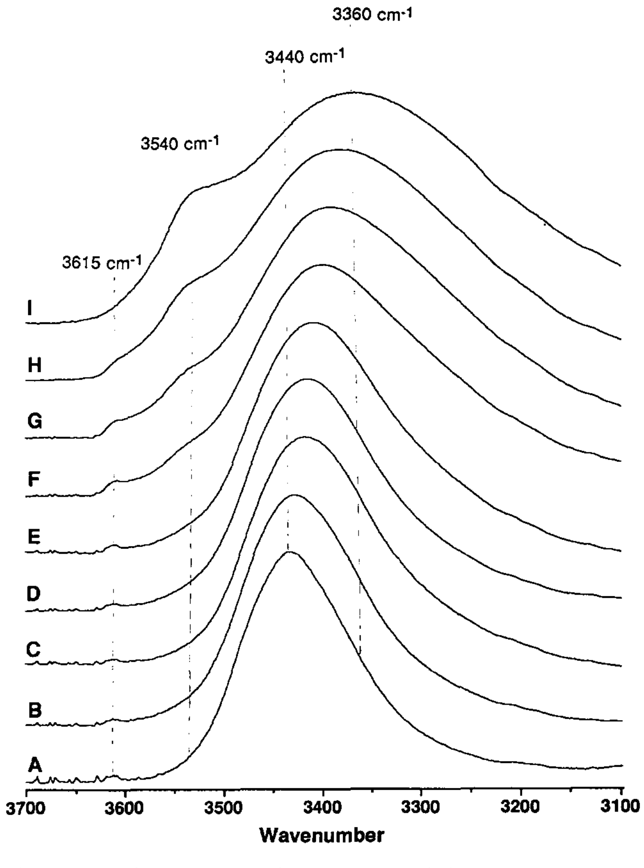


Figure 8 Scale-expanded *FT*i.r. spectra recorded at room temperature in the hydroxyl stretching region for DMAVPh copolymers containing (A) 14, (B) 22, (C) 40, (D) 43, (E) 56, (F) 77, (G) 85, (H) 93 and (I) 100 mol% VPh

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* The spectrum was recorded at room temperature, which is below the glass transition temperature of PVPh ($T_g \approx 170°C$). Accordingly, the frequency of the peak maximum and the precise shape of the hydrogen-bonded envelope will depend upon sample preparation and thermal history

maximum frequency shifts to higher wavenumbers. At the same time the relative intensity of the 'free' hydroxyl band at 3540 cm^{-1} decreases and is barely detected in the copolymers containing >44 mol% DMA. This reflects the new distribution of hydrogen-bonded moieties resulting from the competition between hydroxyl–hydroxyl and hydroxyl–carbonyl specific interactions. From equilibrium considerations we know that in DMA-rich copolymers the latter predominates[1], which infers that the hydroxyl stretching vibration attributed to the OH···O=C interaction occurs at about 3440 cm^{-1}. Note also that in the spectra of the VPh-rich copolymers an additional weak band is detected at approximately 3615 cm^{-1}. This band is attributed to 'free' hydroxyl groups existing in an essentially hydrocarbon environment. Corroboration of this assignment is found in the following infra-red temperature studies of the DMAVPh copolymers.

Figure 9 shows infra-red spectra recorded in the hydroxyl stretching region as a function of temperature for two DMAVPh copolymers containing 56 and 85 mol% VPh (denoted A and B, respectively). These spectra are displayed on *absolute absorbance* scales and, in common with the spectral changes observed in pure PVPh and phenoxy polymers[1,2], the peak maximum of the hydrogen-bonded hydroxyl band shifts significantly to higher frequency and dramatically decreases in intensity as temperature is increased. This is a complex phenomenon and, as we have discussed previously, primarily a manifestation of three factors: changes in the relative concentrations of 'free' and hydrogen-bonded hydroxyl groups; changes in the distribution of the hydrogen-bonded multimers; and changes in the absolute absorptivity as a function of frequency and temperature[1]. Observe that there are two distinct 'free' hydroxyl stretching bands at 3615 and 3540 cm^{-1} in the spectra of the VPh-rich DMAVPh copolymer (B), which increase in intensity with temperature, but remain at essentially constant frequencies. Note also that the former band dominates over the latter when the concentration of DMA in the copolymer is increased (A). As suggested above, this is a manifestation of the relative fraction of isolated hydroxyl groups that interact with phenyl rings (O–H···π interactions) or find themselves surrounded by aliphatic groups and are hence in an essentially non-interacting environment. Corroboration is seen in analogous dilute solution spectra of phenol in cyclohexane (*Figure 8* curve C) and toluene (*Figure 8* curve D) where the 'free' bands are observed at approximately 3548 and 3620 cm^{-1}, respectively. In mixed solvent studies both infra-red bands are observed[18].

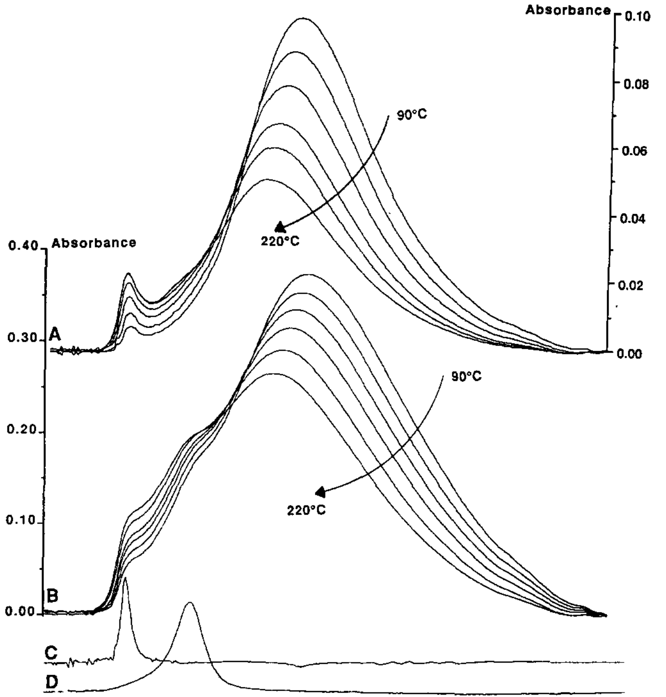

Figure 9 *FT*i.r. spectra recorded as a function of temperature on an absolute absorbance scale in the hydroxyl stretching region for DMAVPh copolymers containing (A) 56 and (B) 85 mol% VPh; and *FT*i.r. spectra of dilute phenol solutions (0.002 M) in (C) cyclohexane and (D) toluene at room temperature

Glass transition temperatures of the AMAVPh copolymers have been reported elsewhere[17] and were found to be significantly higher than the theoretical values calculated using the Fox equation[19]. This positive deviation is attributed to the presence of strong specific interactions (hydrogen bonds)[20]. Thermal stability of the AMAVPh copolymers was studied by *FT*i.r. and thermal gravimetric analysis (t.g.a.). The copolymers appear to be stable in air up to temperatures of 220°C. Infra-red spectra recorded in the carbonyl stretching region of samples cycled up and down are reproducible within error at any particular temperature. This is not the case, however, if samples are exposed to temperatures above 240°C for any appreciable time period. However, no significant weight loss was observed by t.g.a. until about 330°C in air. A DMAVPh copolymer containing 56 mol% VPh was heated at 240°C for 4 h and no significant weight loss was observed. This suggests that transesterification does not take place at temperatures below 240°C. Any transesterification would be indicated by a substantial loss of molecular weight as the product, decyl alcohol, evaporates.

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