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A study of the cyclotrimerisation and polymerisation of aryl cyanates using ^{13}C and ^{15}N nuclear magnetic resonance spectroscopy, fourier transform infra-red spectroscopy and differential scanning calorimetry

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Summary

Three aryl cyanates, together with the products of the cyclotrimerisation of the cyanates to form aryloxy–*s*–triazines, have been characterised by ^{13}C and ^{15}N nmr spectroscopy. A quantitative nmr technique is proposed which allows the monitoring of the conversion of both monofunctional and difunctional cyanates to the corresponding triazines. The results compare favourably with those obtained using Fourier transform infra–red spectroscopy (FTIR) and differential scanning calorimetry (DSC) techniques.

Introduction

Cyanate ester resins are, by virtue of their favourable properties (high Tg, good toughness, low moisture uptake and low overall cure shrinkage), becoming increasingly important in several technological areas such as the aeronautical, automotive and electronics industries. They are formed by a thermal cyclotrimerisation reaction which may be accelerated by transition metal catalysts such as the carboxylates of copper, cobalt or zinc and an active hydrogen donor such as an involatile phenol. The aryloxy–*s*–triazine ring structure so formed will then become part of a cross–linked polycyanurate network if the cyanate monomer is either di– or poly–functional.

Several studies have been carried out on the homopolymerisation of aryl cyanates (1–4) and the most widely postulated mechanism for the stepwise formation of the cyclotrimer proposes that the metal catalyst coordinates to the cyanate molecules in such a way as to enhance the opportunity for forming the cyanurate ring. Ring closure can then proceed via an imidocarbonate intermediate (Scheme 1) or perhaps by an anion–initiated mechanism.

Although work on the synthesis of aryl cyanates has been the subject of several publications (5–7) it is only recently with improved synthetic procedures (8,1) that pure materials have become available (9). This has made possible several x–ray structure studies (10,11) as well as kinetic investigations of the thermal polymerisations (11,12). In the latter area the experimental techniques used have usually been Fourier Transform infra–red spectroscopy (FTIR) (13,1) and differential scanning calorimetry (DSC) (14–16) both of which have certain limitations. For the arylcyanates ^{15}N nmr spectroscopy offers an attractive alternative as the low sensitivity of this nuclide is no longer a serious problem given the improvements in magnet design that have taken place during the last decade (17) Furthermore the inherent simplicity of the spectra – a single chemical shift signal for the cyanate monomer and two easily discernible signals in the partly converted mixture – greatly simplifies the interpretation of the results.

The present study was therefore primarily undertaken to see whether ^{15}N nmr spectroscopy could be used to monitor the degree of conversion of the cyanate monomer and to compare the results with those obtained using FTIR, DSC and ^{13}C nmr spectroscopy. The task was simplified by the knowledge that the ^{15}N nmr assignments had already been made for a number of alkyl and aryl cyanates

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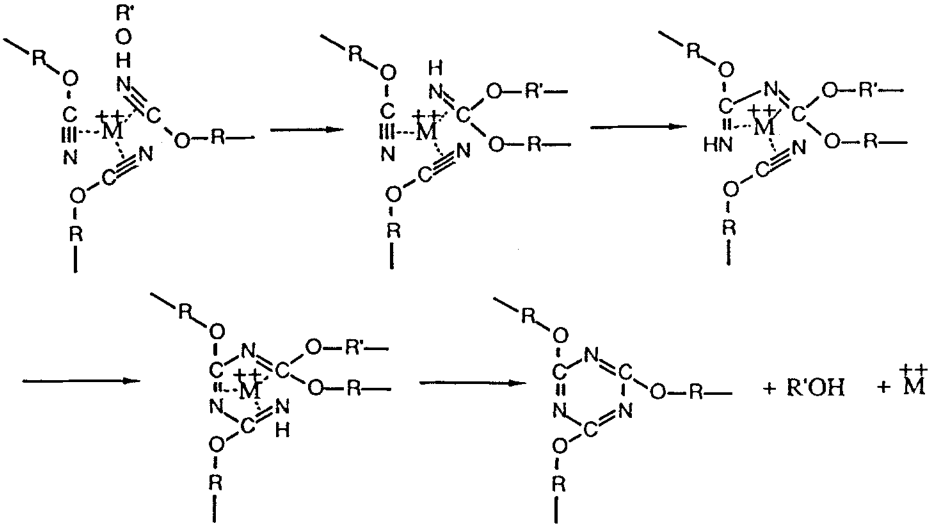


Scheme 1

(17,18,19) although the use of heteronuclear techniques, which could be of great use in monitoring the changing environment of the cyanate and triazine functional groups, has not as yet been fully explored. This research is not unrelated to a recent study which determined the molecular weight of non–linear polymers using ^{13}C nmr spectroscopy (20). There remains the possibility of potential for ^{15}N nmr in that context as well, and work continues to clarify this point (11).

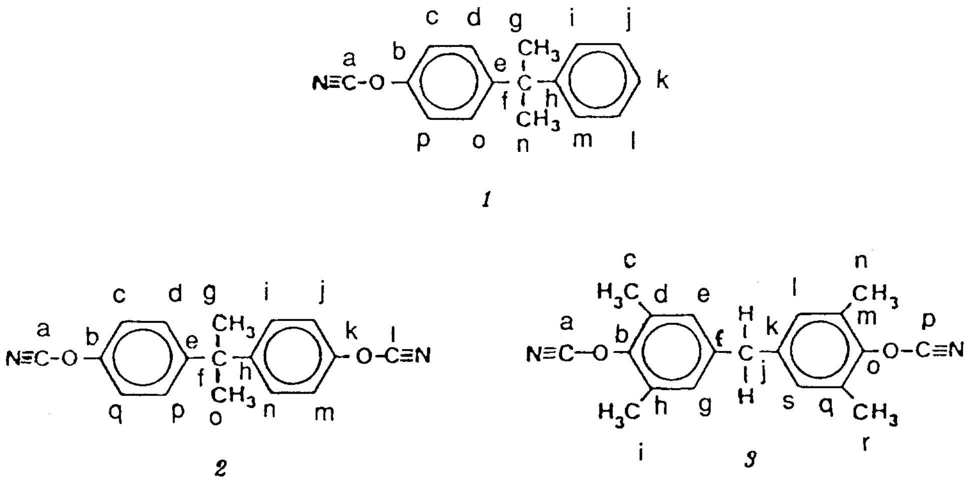
Experimental

Infra–red spectra were recorded on a Perkin–Elmer 1750 FTIR spectrometer interfaced to a Perkin–Elmer 7300 computer; the samples were presented either as thin films or KBr discs.

Nuclear magnetic resonance spectra were recorded at 298K using a Bruker AC–300 spectrometer operating at 75.5 MHz for ^{13}C and 30.4 MHz for ^{15}N. ^{13}C spectra were recorded in d$_6$–acetone solvent whilst samples for ^{15}N nmr were dissolved in acetone prior to adding chromium (III) acetylacetonate (at an approximate concentration of 15 mg per 0.02 mole of nitrogen) (17) so as to eliminate Nuclear Overhauser Effects and reduce relaxation times. The ^{13}C nmr chemical shifts are reported relative to tetramethylsilane and the ^{15}N nmr chemical shifts relative to external nitromethane. ^{13}C–^{1}H two dimensional correlation spectra were recorded using well established literature procedures.(21–23).

Differential scanning calorimetry was performed at 10°C/min under nitrogen (40 ml/min) using a Du Pont 910 calorimeter interfaced to a Du Pont 9900 computer/thermal analyser. Samples (2–3 mg) were run in sealed aluminium pans at a variety of heating rates. Where analysis of the prepolymers revealed a significant disparity in the baseline before and after the polymerisation exotherm, a sigmoidal baseline algorithm (developed in–house) (24) was used.

Three aryl cyanates (*1–3*) were used in the present study. The prepolymers of *2* and *3* (*2p*,*3p*) were used as supplied. The fully cured *s*–triazine product of the polymerisation of 2–phenyl–2–(4–cyanatophenyl)isopropylidene (*1c*) was prepared by heating *1* with a trace of AlCl$_3$ at 180°C under nitrogen for 45 min (8). The partially cured product (*1a*) was prepared by heating *1* with a trace of AlCl$_3$ at 180°C under nitrogen for 5 min; (*1b*) was prepared by heating *1* (without catalyst) for 24 hrs (see Table 1).



1 *2* *3*

Scheme 2
Monomers studied in this work

Table 1: Nominal fractional conversions of the compounds studied

Compound	Conversion	Compound	Conversion	Compound	Conversion
1	0	*2*	0	*3*	0
1a	30	*2p*	30	*3p*	30
1b	60				
1c	100				

Results

In the infra-red work a reference sample of each unreacted monomer (*1*–*3*) was analysed together with samples containing progressively larger fractions of reacted cyanate. The cyanate group displays a characteristic intense doublet centred at 2230 and 2270 cm^{-1} (1) and these signals are reduced as the cyclotrimerisation reaction proceeds (while signals at 1565 and 1365 cm^{-1} corresponding to the triazine ring and cyanurate stretching vibrations increase). The intensity of the cyanate band at 2270 cm^{-1} is compared with a signal that is constant throughout the polymerisation e.g. the C–H stretching vibration of a methyl group at 2875 cm^{-1}. The ratio of the intensities of the cyanate and the methyl group signals is then calculated for both the monomer and polymer. In each case baselines were drawn for the respective 2270 and 2875 cm^{-1} absorbance peaks and the peak heights measured. A normalised absorbance Y was obtained as the ratio of the absorbance height at 2270 cm^{-1} to the absorbance peak height at 2875 cm^{-1} for each spectrum. The percentage of unreacted cyanate remaining in the cured homopolymer was then calculated relative to the cyanate content of the monomer as $\alpha = 1 - (Yc/Ym)$ where Yc = normalised absorbance of the cured material and Ym = normalised absorbance of the monomer. Figure 1 shows a series of partial infra-red spectra for progressively-cured samples of *1*.

In the DSC experiments the degree of conversion α is taken as $\alpha = 1 - (\Delta H_C/\Delta H_m)$ where ΔH_C = polymerisation enthalpy of cured material and ΔH_m = polymerisation enthalpy of monomer. Typical thermograms are given in Figure 2.

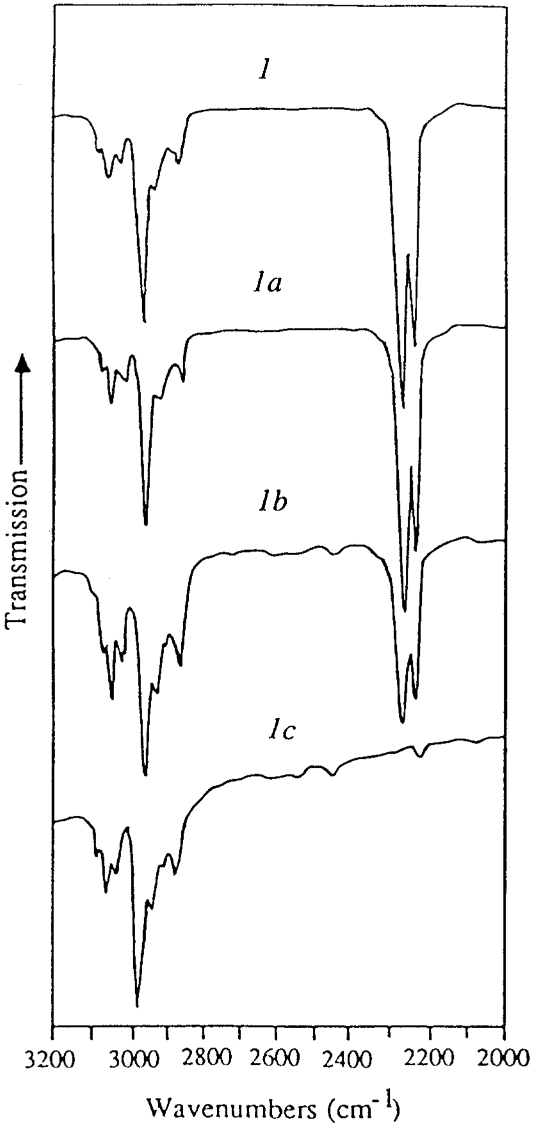


Figure 1 Partial infra-red spectra for progressively-converted *1*

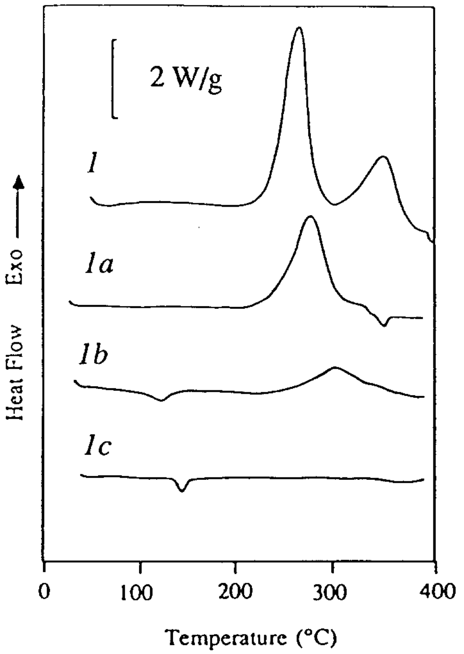


Figure 2 Dynamic DSC thermograms (10K/min. under nitrogen) for progressively-converted *1*

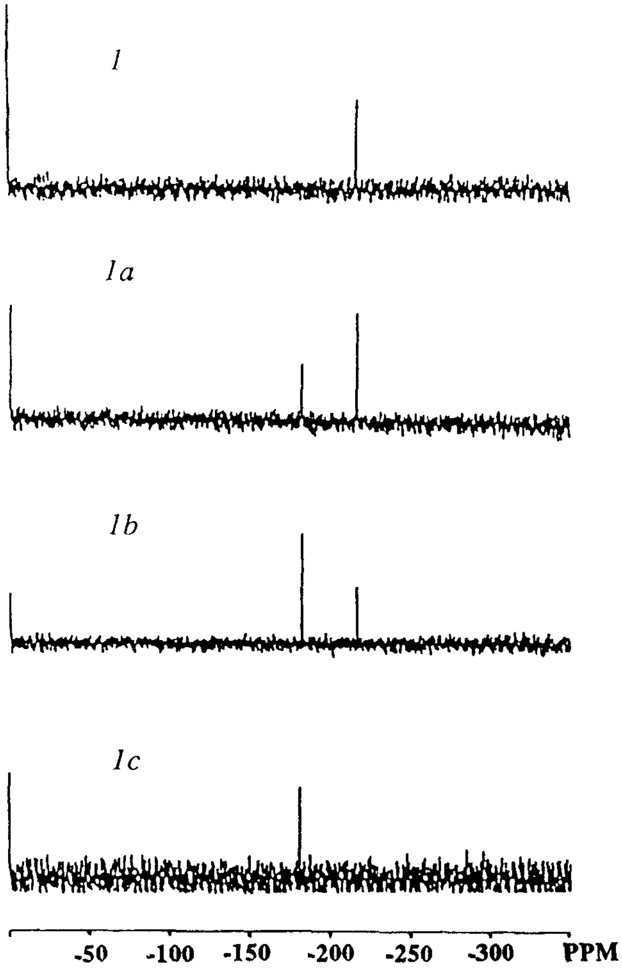


Figure 3 ^{15}N nmr spectra for progressively-converted *1* (nitromethane external standard).

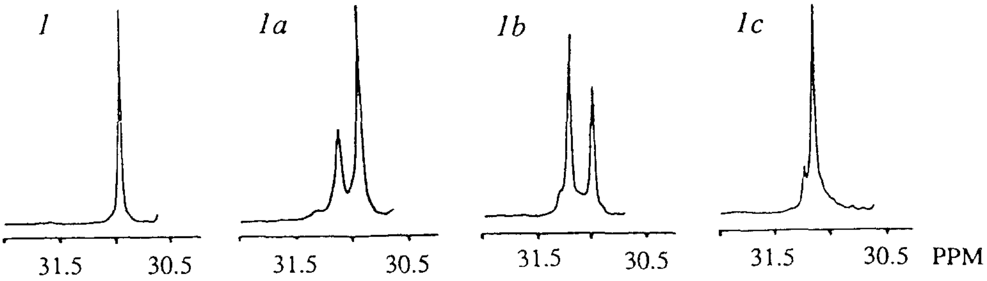


Figure 4 Partial ^{13}C nmr spectra for progressively-converted *1*.

The ^{15}N nmr spectra of all the partially cured materials are very simple, consisting of two well–separated signals, which under the experimental conditions, are directly proportional to the concentration of the species present in the mixture. The degree of conversion is given by $\alpha = [1 - I_c/(I_c + I_t)]$ where I_c is the cyanate signal intensity and I_t the triazine signal intensity. Figure 3 gives ^{15}N nmr spectra of progressively–cured samples of *1*.

The ^{13}C nmr spectra are considerably more complex then the ^{15}N nmr spectra and the proposed method for calculating the degree of conversion depended on selecting a carbon atom that does not particulate in the reaction mechanism and is present in both the monomer and partially (or entirely) cured product. In the case of compound *3* the methyl carbons (C_c, C_i, C_n and C_r) were chosen, and as can be seen in the ^{13}C nmr spectrum of the prepolymer (Figure 4) the methyl carbons are in sufficiently different environments as to appear as two discrete signals. Compounds *1* and *2* were treated in the same manner using methyl carbons C_g and C_n, and C_g and C_o respectively, as non–participating carbons. The degree of conversion α is then given by $\alpha = [1 - (I_{mm}/(I_{mm} + I_{mc})]$ where I_{mm} is the intensity of the methyl carbon in the monomer and I_{mc} the intensity of the methyl carbon in the cured material.

The ^{15}N and ^{13}C nmr chemical shifts of the three cyanate monomers, together with their assignments, are given in Table 2.

Table 2: Assignment of ^{13}C and ^{15}N nmr spectra of the cyanate monomers (*1*–*3*)

Compound *1*		Compound *2*		Compound *3*	
Chemical Shift (ppm)	Assignment	Chemical Shift (ppm)	Assignment	Chemical Shift (ppm)	Assignment
151.86	C_b	151.99	C_b,C_k	150.70	C_b,C_o
150.71	C_h	149.85	C_e,C_h	141.59	C_f, C_k
150.64	C_e	129.84	C_d,C_i,C_n,C_p	130.99	C_e,C_g,C_l,C_s
129.88	C_j,C_l	115.75	C_c,C_j,C_m,C_q	129.53	C_d,C_h,C_m,C_q
128.97	C_d,C_o	109.43	C_a,C_l	110.96	C_a,C_p
127.38	C_k	43.22	C_f	40.64	C_j
126.68	C_i, C_m	30.89	C_r,C_o	15.40	C_c,C_i,C_n,C_r
115.56	C_c,C_p				
109.53	C_a				
43.35	C_f				
30.94	C_g,C_n				
–215.36	N_a	–214.98	N_a,N_l	–225.63	N_a,N_p

Discussion

The degrees of conversion (α) expressed as a percentage for both the monofunctional cyanate (*1*) and the two commercial dicyanates (*2*,*3*) as determined using the four different methods are presented in Table 3. With the possible exception of the ^{13}C nmr results for compound *1*, where the α values are lower than those determined by the other experimental methods, good agreement exists between the results obtained by FTIR, DSC, ^{15}N nmr and ^{13}C nmr spectroscopy. The inherent simplicity of the ^{15}N nmr spectra may offer advantages over the corresponding ^{13}C nmr spectroscopy method in cases where the latter spectra are more complex than in the current examples. The development of solid state nmr techniques may also be of assistance in cases where the polymers are very sparingly soluble.

Table 3: Degrees of conversion (α) for the three cyanates as determined by different experimental methods

	^{15}N NMR			^{13}C NMR			FTIR			DSC	
Sample	δ (ppm)	Int.	α(%)	δ (ppm)	Int.	α(%)	Y_c	Y_m	α(%)	ΔH (J/g)	α(%)
1	−215.36	11.154	0	30.94	21.626	0	6.313	6.313	0	420.3	0
1a	−215.35 −180.60	11.025 5.680	34	30.90 31.10	8.435 3.670	30	4.040	6.313	36	273.2	35
1b	−215.32 −180.84	5.884 11.238	66	30.89 31.11	3.701 5.291	59	2.175	6.313	66	128.6	68
1c	−180.39	11.542	100	30.97 31.14	1.138 16.845	94	0.000	6.313	100	3.2	99
2	−214.98	11.655	0	30.89	11.302	0	3.850	3.850	0	773.4	0
2p	−215.19 −180.62	15.479 6.328	29	30.90 31.09	8.433 3.668	30	2.815	3.850	27	503.2	35
3	−225.63	11.019	0	15.59	15.401	0	3.952	3.952	0	649.1	0
3p	−225.66 −183.10	11.048 3.458	24	15.57 16.28	16.030 5.087	24	2.723	3.952	31	493.5	24

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