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Polyol Structural Elucidation in Binder Polyesters

1. ^{13}C NMR Study of Fundamental Polyols in Aliphatic and Aromatic Polyesters

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SUMMARY

An extensive number of polyesters containing various fundamental binder polyols: linear glycols, 2,2-disubstituted 1,3-propanediols, branched glycols, and tri- and tetrafunctional alcohols have been prepared with mono- and dibasic aliphatic and aromatic acids. The ^{13}C NMR investigation of all these polyesters in $CDCl_3$ furnishs comprehensive chemical shift information of the constituting polyol structures. The data not only allow a definite identification of the polyols but also disclose whether a particular polyol structure is in fully condensed aliphatic or aromatic surroundings.

INTRODUCTION

Polyesters constitute more than one third of the synthetic binders employed by the coatings industry. The extensive use of polyesters is basically due to potentially wide variations in composition resulting in quite different properties and performance. This is partly accomplished by incorporating mixtures of di-, tri- or multifunctional alcohols (polyols) into these polyesters in addition to different (polybasic) acids including the important fatty acids. In fact, experience from the coatings field tells that binder polyesters with few exceptions are at least four-component polyesters, even when the frequently used fatty acid mixtures are considered as one component only.

Traditional, compositional polyester analyses involve hydrolysis followed by derivation allowing the constituted acids and polyols to be determined by gas chromatography as methyl esters and polyol acetates respectively (IUPAC 1973). Although these methods result in overall determinations, they provide no sequencial monomer distribution and thus no structural information due to their inherently destructive nature.

^{13}C NMR spectroscopy has already manifested itself as a powerful structure determining tool for polyesters. Recently KRICHELDORF (1978) showed that the chemical shifts of linear diols in polyesters are influenced by the type and size of the constituting diacid. In addition the possibilities for ^{13}C analysis of four-component polyesters were indicated. These findings are later elaborated by NEWMARK (1980) and RUSSELL et al. (1981) who describe detailed analyses of a three- and a four-component polyester respectively. These ^{13}C analyses, however, cover only a very limited number of diols including only a couple of the frequently used glycols in binder polyesters, and are, therefore, clearly insufficient for comprehensive ^{13}C analysis. The investigated polyesters also differ significantly from typical binder polyesters due to the linear structure and relatively high molecular weight necessitating powerful solvents such as trifluoroacetic acid to obtain tractable solutions. Binder polyesters on the other hand often have a considerable amount of functional groups (e.g. hydroxyl) and relatively low molecular weight with solubility in less exotic solvents e.g. chloroform as a result.

Consequently, the aim of the present work is a systematic ^{13}C NMR study of the commonly used polyols in binder polyesters in well-defined environments. The ultimate goal is an analytical method which allows us not only to determine polyester consitituents, but also the ratio between the structural units. This then would become a unique tool in the development and evaluation of new polyester resins with improved properties. The apparent lack of comprehensive basic information and the interest expressed when the initial results were presented (HVILSTED 1982), have prompted us to publish our initial findings.

EXPERIMENTAL

Preparation of model polyesters.

Model polyesters of the basic polyols in well defined surroundings were prepared from the polyols according to TABLE I in approximately 10 g batches. Generally synthetic grade or better grade chemicals, if available, were used as received in all preparations.

Polyol acetates (Ac) were synthesized by reacting the respective polyol with an excess of acetyl chloride (eq. 1). When complete reaction was assured after appropriate refluxing, depending on the type of polyol employed, the excess of acetyl chloride was distilled off.

Polyadipates (Adip) and polyisophthalates (Iso) were achieved by mixing equivalent amounts of glycol and dimethyl adipate or dimethyl isophthalate respectively with catalytic quantities of NaOH and PbO (eqs. 2 and 3). The

TABLE I
Preparation of model polyesters

Aliphatic (Al)

Polyol acetates:

$$HO\text{-}R\text{-}OH \;+\; ClCOCH_3 \;\longrightarrow\; \underset{(Ac)}{CH_3COO\text{-}R\text{-}OOCCH_3} \;+\; HCl\uparrow \qquad (1)$$

Polyadipates:

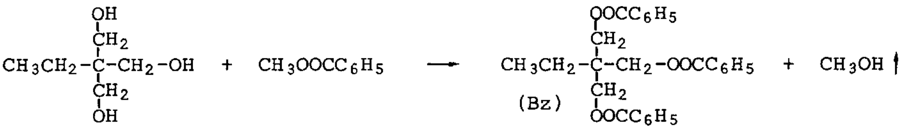
$$HO\text{-}R\text{-}OH \;+\; CH_3OOC(CH_2)_4COOCH_3 \;\longrightarrow\; \underset{(Adip)}{\left(O\text{-}R\text{-}OOC(CH_2)_4CO \right)_n} \;+\; CH_3OH\uparrow \qquad (2)$$

Aromatic (Ar)

Polyisophthalates:

$$HO\text{-}R\text{-}OH \;+\; CH_3OOCC_6H_4COOCH_3 \;\longrightarrow\; \underset{(Iso)}{\left(O\text{-}R\text{-}OOCC_6H_4CO \right)_n} \;+\; CH_3OH\uparrow \qquad (3)$$

Benzoates:



$$CH_3CH_2\text{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{\overset{CH_2}{\underset{CH_2}{C}}}}\text{-}CH_2\text{-}OH \;+\; CH_3OOCC_6H_5 \;\longrightarrow\; CH_3CH_2\text{-}\overset{\overset{OOCC_6H_5}{|}}{\underset{\underset{OOCC_6H_5}{|}}{\overset{CH_2}{\underset{CH_2}{C}}}}\text{-}CH_2\text{-}OOCC_6H_5 \;(Bz) \;+\; CH_3OH\uparrow \qquad (4)$$

transesterification was accomplised by heating while passing a slow stream of nitrogen gas through the molten mixture. The nitrogen stream resulted in some stirring and assisted the simultaneous distillation of the evolved methanol. The reaction was stopped by cooling when extensive polymerization had occured as judged from a considerable increase in the viscosity of the reaction mixture.

Benzoates (Bz) of the tri- and tetrafunctional polyols were prepared in a similar transesterification with excess of methyl benzoate (eq. 4). When no further methanol distilled off, the bulk of the excess of methyl benzoate was removed from the products by distillation.

All polyester models were analysed as they appeared after the indicated work up without any further purification.

^{13}C NMR spectra.

The ^{13}C NMR spectra were recorded at room temperature on a Jeol FX 60 Q FT-NMR spectrometer with an operating frequency of 15.0 MHz. Spectra were acquired on 0.5 g samples in 2 ml $CDCl_3$ with TMS in 10 mm diameter tubes. A pulse width of 6 µs (approx. 45^0) and a 1.5 s pulse repetition time was used to obtain normally 1000 scans accumulated with 8K data points on a spectral width of 3000 Hz.

RESULTS and DISCUSSION

Polyadipates are choosen as models for aliphatic acid parts because the adipate is frequently met in binder polyesters. Furthermore KRICHELDORF (1978) showed, that aliphatic chains longer than tetramethylene as in adipate, had no additional ^{13}C chemical shift effect on glycols in polyesters. Consequently the aliphatic chain in adipate is long enough to serve as a model for fatty acids as well. Polyisopthalates are selected as models for the aromatic acids since isopthalate likewise often is found in polyester binders. The numerous prepared model polyesters were all characterized by both ^{1}H and ^{13}C NMR spectroscopy. However, the information derived from ^{13}C spectroscopy appears to be extremely detailed and much superior in structural respect. For that reason we are reporting the ^{13}C chemical shift information originating from the polyol structures, which is extracted and compiled in TABLES II to V.

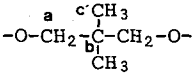
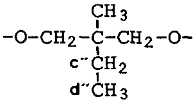
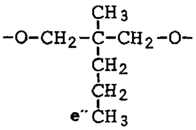
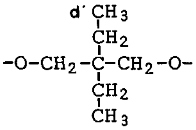
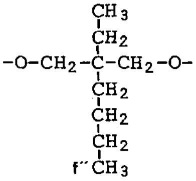
The results of the considered polyols are organized into four groups according to structure under the parent headings: linear glycols, 2,2-disubstituted 1,3-propanediols, branched glycols, and polyols (tri-and tetrafunctional alcohols). In the respective TABLES II to V only the polyol structures are shown, and the abbreviations of the particular environments refer to the symbolism of TABLE I. Thus Al is representing aliphatic models either polyol acetates (Ac) or polyadipates (Adip), and similarly Ar corresponds to the aromatic models either polyisophthalates (Iso) or benzoates (Bz). The letters heading the chemical shift values refer to the structures in the following way. "a", "b", "c" generally denote carbons in the main chain of the polyol unit and reflect the distance in increasing order to the nearest ester oxygen atom, thus "a" corresponds to a α-position, "b" to a β-position etc. "c´", "d´" denote carbons in the shortest branch and "c´´", "d´´", "e´´", and "f´´" refer to carbons in the longest branch, where "c´" and "c´´" correspond to γ-positions to the nearest ester oxygen atom, "d´" and "d´´" correspond to δ-positions and so on. Symmetrical carbons are not indicated on the structures in the TABLES and are either deleted in the chemical shift columns or marked with a dash to avoid confusion.

TABLE II
^{13}C Chemical shifts and peak assignments of linear glycols in polyesters, ppm relative to internal TMS in $CDCl_3$

Glycol structure	Environment		Carbon		
			a	b	c
a $-O-CH_2-CH_2-O-$	Al	(Ac)	61.9		
		(Adip)	61.8		
	Ar	(Iso)	62.8		
a b $-O-CH_2-CH_2-O-CH_2-CH_2-O-$	Al	(Ac)	63.0	68.7	
		(Adip)	63.0	68.7	
	Ar	(Iso)	64.0	68.9	
a b c $-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-$	Al	(Ac)	63.2	68.9	70.3
	Ar	(Iso)	64.1	68.9	70.5
a b $-O-CH_2-CH_2-CH_2-O-$	Al	(Ac)	60.5	28.1	
	Ar	(Iso)	61.9	28.3	
a b $-O-CH_2-CH_2-CH_2-CH_2-O-$	Al	(Ac)	63.5	25.4	
		(Adip)	63.5	25.3	
	Ar	(Iso)	64.6	25.6	
		(Bz)	64.3	25.7	
a b c $-O-CH_2-CH_2-CH_2-CH_2-CH_2-O-$	Al	(Ac)	63.7	28.3	22.5
	Ar	(Iso)	64.8	28.4	22.6
a b c $-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O-$	Al	(Ac)	63.8	28.5	25.6
	Ar	(Iso)	64.9	28.6	25.7

TABLE II lists the obtained results of the linear glycols: ethylene glycol (1,2-ethanediol), diethylene glycol (3-oxa-1,5-pentanediol), triethylene glycol (3,6-dioxa-1,8-octanediol), 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol. This TABLE shows that each glycol structure is characterized by sets of chemical shifts, which allows identification of these glycols in polyesters by ^{13}C NMR. Since virtually no differences are observed between the chemical shifts of a particular glycol structure in the polyol acetate (Ac) and in the corresponding polyadipate (Adip), the polyol acetates generally are adequate models for glycol structures in aliphatic polyesters. This is not only an advantage in the easier preparation of the models, but it prevents the sometimes unavoidable and well known formation of ether between the glycols leading to diglycols during a high temperature transesterification. The "a" carbons of the glycol structures on the other hand are consistently deshielded by approximately 1 ppm more in the polyisophthalates as compared to the corresponding aliphatic polyesters. Recent investigations, however, have shown (HVILSTED and JØRGENSEN 1983) that even larger deshielding effects are obtained on the "a" carbons of these glycols in polyorthophthalates. Consequently the particular type of aromatic acid should be considered, and no general statement of aromatic influence other than the already discussed can be made. The difference between the two aromatic models (Iso) and (Bz) of 1,4-butanediol substantiate this. The remaining carbons of the linear glycol struc-

TABLE III
^{13}C Chemical shifts and peak assignments of 2,2-disubstituted 1,3-propanediols in polyesters, ppm relative to internal TMS in $CDCl_3$

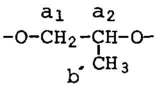
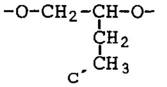
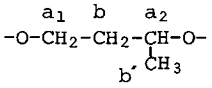
Diol structure	Environment	Carbon a	b	c′	c″	d′	d″	e″	f″
 $-O-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-O-$	Al (Ac)	69.0	34.6	21.6	-				
	Al (Adip)	68.9	34.7	21.7	-				
	Ar (Iso)	70.0	35.5	21.9	-				
 $-O-CH_2-\overset{CH_3}{\underset{CH_2CH_3}{C}}-CH_2-O-$	Al (Ac)	67.4	37.1	18.5	27.0		7.5		
	Ar (Iso)	68.5	38.0	18.9	27.5		7.7		
 $-O-CH_2-\overset{CH_3}{\underset{CH_2CH_2CH_3}{C}}-CH_2-O-$	Al (Ac)	67.8	37.2	19.1	37.2		16.5	14.8	
	Al (Adip)	67.7	37.3	19.2	37.3		16.5	14.8	
	Ar (Iso)	68.8	38.0	19.5	37.5		16.6	14.9	
 $-O-CH_2-\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}-CH_2-O-$	Al (Ac)	65.5	39.4	23.6	-	7.2	-		
	Ar (Iso)	66.8	40.3	24.2	-	7.4	-		
 $-O-CH_2-\overset{CH_2CH_3}{\underset{CH_2CH_2CH_2CH_3}{C}}-CH_2-O-$	Al (Ac)	65.8	39.4	23.4	30.9	7.3	24.9	24.2	13.8
	Ar (Iso)	67.3	40.3	23.5	30.5	7.3	25.0	24.7	13.9

tures are only marginally affected by the different environments, adipate and acetate or isophthalate. An obvious explanation seems to be the increased distance between the carbons of interest ("b" and "c") and the influencing acid structures compared to the situation existing in the "a" case, causing the ^{13}C substituational effects to diminish to only marginal differences.

TABLE III contains the corresponding information for a series of 2,2-disubstituted 1,3-propanediols beginning with neopentyl glycol, the dimethyl derivative, and additionally including derivatives with methyl-ethyl, methyl-n-propyl, diethyl, and ethyl-n-butyl substitution. This information also allows these 1,3-propanediol structures to be identified in polyesters from their characteristic and unique ^{13}C spectra. In this series two examples (dimethyl and methyl-n-propyl) confirm the previously discussed similarity of polyol chemical shifts in polyesters containing adipate or acetate. The "a" carbons of the 1,3-propanediol structures in the polyisophtalates are similarly deshielded compared to the aliphatic analogues. However, the deshielding here appears to increase from 1,1 ppm in case of the smallest 1,3-propanediols up to 1.5 ppm for the largest member. Additionally the "b" carbons (Iso) experience considerable deshieldings in comparison

TABLE IV

^{13}C Chemical shifts and peak assignments of branched glycols in polyesters, ppm relative to internal TMS in $CDCl_3$

Glycol structure	Environment	Carbon				
		a_1	a_2	b	b′	c′
 $-O-\overset{a_1}{CH_2}-\underset{\underset{b'}{CH_3}}{\overset{a_2}{CH}}-O-$	Al (Ac)	65.9	68.1		16.5	
	Al (Adip)	65.7	67.9		16.5	
	Ar (Iso)	66.6	69.2		16.6	
 $-O-CH_2-\underset{\underset{\underset{c'}{CH_3}}{CH_2}}{CH}-O-$	Al (Ac)	64.5	72.6		24.0	9.4
	Ar (Iso)	65.4	73.7		24.1	9.5
 $-O-\overset{a_1}{CH_2}-\overset{b}{CH_2}-\underset{\underset{b'}{CH_3}}{\overset{a_2}{CH}}-O-$	Al (Ac)	60.2	67.3	34.8	19.9	
	Al (Adip)	60.4	67.6	35.0	20.0	
	Ar (Iso)	61.8	69.3	35.4	20.7	

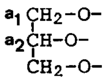
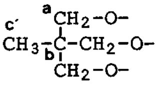
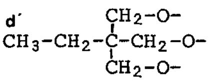
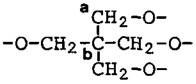
with (Adip) or (Ac) in the order of 0.7-0.9 ppm in contrast to the marginal effects of "b" carbons in the linear glycols including the unsubstituted 1,3-propanediol. The twofold influence from equally distant isophthalic structures can not satisfactorily explain this behaviour, since 1,3-propanediol ((Iso) TABLE II) has the exact same substitution without noticeable contribution to the deshielding. More likely, the quarternary nature of these "b" carbons with attached bulky substituents in combination with the rather stiff isophthalic structures in close proximity is influenced by some kind of conformational effects not exerted in the unsubstituted analogue. Further support for the conformational effect concept is obtained from the noticeable deshielding (0.1-0.6 ppm) of the "c′" and "c′′" carbons (Iso) in the side groups, since previously "c" carbons influenced by two equivalent acid structures exhibited only marginal effects (0.1 ppm in 1,5-pentanediol, TABLE II).

TABLE IV lists the results of the branched glycols: propylene glycol (1,2-propanediol), 1,2-butanediol, and 1,3-butanediol. The important achievement again is the possiblility to identify these glycols in polyesters based on the ^{13}C spectra. The "a_1" and "a_2" carbons in (Iso) also here appear to be deshielded as already throughly discussed. Some of the remaining carbons are only marginally effected ("b′" and "c′" in (Iso) of propylene glycol and 1,2-butanediol), while the rest are appreciably influenced ("b" and "b′" in (Iso) of 1,3-butanediol). The apparent diverse trends are probably due to the actual difference in structure between these glycols although the tertiary carbon with alkyl substitution is a common feature. Consequently possible conformational effects could have a different impact.

TABLE V contains the information of the multifunctional alcohols: glycerol, trimethylolethane (2-methyl-2-(hydroxymethyl)-1,3-propanediol), trimethylolpropane (2-ethyl-2-(hydroxymethyl)-1,3-propanediol), and pentaerythritol, as the completely condensed acetates and benzoates. The quite different influence on the ^{13}C chemical shifts of the polyol structures caused by aliphatic and aromatic acid structures here exemplified by (Ac) and (Bz) is again evident. The information, however, appear to be of less practical analytical value, exept maybe for glycerol, because completely esterified structures are not likely to be present in noticeable concentration in binder polyesters with dibasic acids. The progressing condensation during the

TABLE V

^{13}C Chemical shifts and peak assignments of polyols in polyesters, ppm relative to internal TMS in $CDCl_3$

Polyol structure	Environment	Carbon a	b	c′	d′
 $\begin{array}{l} {}^{a_1}CH_2\text{-}O\text{-} \\ {}^{a_2}CH\text{-}O\text{-} \\ \quad CH_2\text{-}O\text{-} \end{array}$		a_1 a_2			
	Al (Ac)	62.0 69.0			
	Ar (Bz)	62.9 69.9			
 $\begin{array}{l} c' \quad {}^{a}CH_2\text{-}O\text{-} \\ CH_3\text{-}\underset{b}{C}\text{-}CH_2\text{-}O\text{-} \\ \quad CH_2\text{-}O\text{-} \end{array}$	Al (Ac)	65.6	38.3	17.0	
	Ar (Bz)	66.6	39.5	17.6	
 $\begin{array}{l} d' \qquad CH_2\text{-}O\text{-} \\ CH_3\text{-}CH_2\text{-}C\text{-}CH_2\text{-}O\text{-} \\ \qquad CH_2\text{-}O\text{-} \end{array}$	Al (Ac)	63.8	40.6	23.3	7.3
	Ar (Bz)	65.1	41.8	24.1	7.6
 $\begin{array}{l} \qquad {}^{a}CH_2\text{-}O\text{-} \\ \text{-}O\text{-}CH_2\text{-}\underset{b}{C}\text{-}CH_2\text{-}O\text{-} \\ \qquad CH_2\text{-}O\text{-} \end{array}$	Al (Ac)	62.2	41.9		
	Ar (Bz)	63.7	43.3		

preparation of this type of polyesters ultimately leads to a cross-linked material which is undesirable in coatings context due to the resulting insolubility. The established ^{13}C differences between the polyol structures in completely condensed aliphatic and aromatic environments, nevertheless strongly suggest that these very important polyols will reveal ^{13}C differences even when incorporated in binder polyesters with less than complete esterification. In fact NEWMARK et al. (1981) observed four peaks from the quarternary carbon of pentaerythritol in the ^{13}C spectrum of a polyester of caprolactone initiated by pentaerythritol. The peaks differed by more than 0.5 ppm and were assigned to polyesters containing three, two, one and no methylol groups respectively. ^{13}C spectra of binder polyesters containing the discussed polyols actually show complex peaks in the regions indicated in TABLE V (HVILSTED and JØRGENSEN 1983).

CONCLUSION

^{13}C NMR investigations of an extensive number of important binder polyols in polyesters have shown that the ^{13}C chemical shifts of the polyol carbons invariably allow all the investigated polyols to be identified in binder polyesters. In addition, the ^{13}C shieldings of the glycol carbons are influenced in different ways by the acid constituents of the polyesters, aliphatic or aromatic, the latter exemplified by isophthalic acid. The influence, however, depends on the type of glycol but is distinctive for the different structural groups of glycols. Furthermore this different influence in all instances enables the characterization of the glycol segments in completely aliphatic and aromatic sequences.

This obtainable ^{13}C information is believed to be an initial prerequisite in the progressing development of a non-destructive analytical method which can provide detailed structural insight into binder polyesters which is impossible to obtain otherwise. This prediction is supported by a ^{13}C NMR study of end groups, especially methylol groups, currently in progress, that shows a similar extreme structure sensitivity.

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