The Mannich bases in polymer synthesis: 3.* Reduction of poly(β-aminoketone)s to poly(γ-aminoalcohol)s and their *N*-alkylation to poly(γ-hydroxy quaternary ammonium salt)s

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(*Received* 6 *April* 1982)

Several poly(β-aminoketone)s, obtained by polyconensation of bis Mannich bases with bis (secondaryamine)s, have been quantitatively reduced to poly(γ-aminoalcohol)s. The stereochemistry of these polymers, as well as that of the reduction products of the parent bis Mannich bases has been investigated. By *N*-alkylation of the same polymers, poly(γ-hydroxy quaternary ammonium salt)s have been also prepared.

Keywords Poly(γ-aminoalcohol)s; poly(quaternary ammonium salt)s; polymeric Mannich bases; reduction; stereochemistry; ^{13}C nuclear magnetic resonance

INTRODUCTION

It is known that several γ-aminoalcohols have stimulated some interest in the pharmaceutical field, for instance their use as analgesics[1] and anti-inflammatory agents[2]. Therefore, we thought it interesting to study a general synthetic route to producing polymers having the structure of poly(γ-aminoalcohol)s. This should be considered a part of a wider research programme on pharmacologically active polymers[3].

Besides their potential pharmacological interest, polymers having a poly(γ-aminoalcohol) structure, as well as other tertiary amino polymers, may have applications in the biomedical field, and also as metal ion complexing agents[4-7].

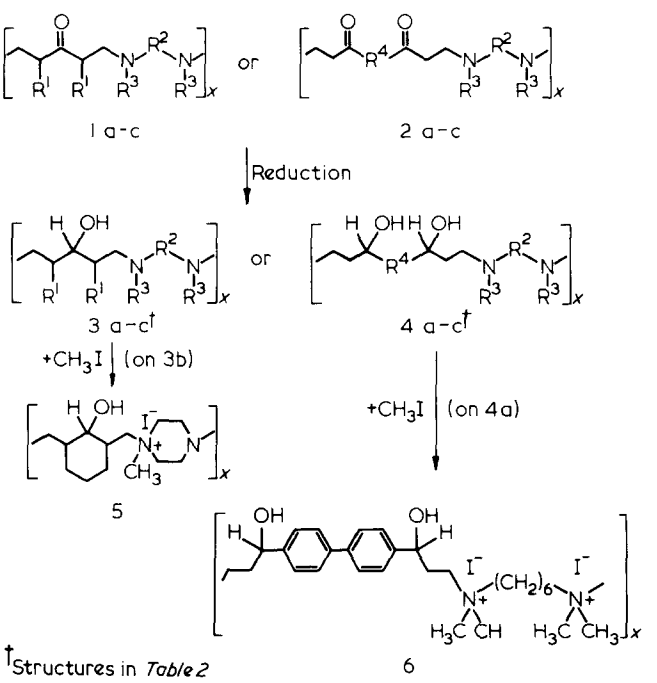
In a previous paper[8] we have reported the synthesis of poly(β-aminoketone)s 1a–c and 2a–c (see *Scheme 1*) by polycondensation of bis(β-dialkylaminoketone)s with bis(secondary amine)s. Here we report on the synthesis of poly(γ-aminoalcohol)s 3a, 3b, 3c and 4a, 4b, 4c by reduction of the above poly(β-dialkylaminoketone)s 1 and 2. For comparison purposes, we have also studied the reduction of some non-macromolecular models. Some data on the stereochemistry of the reduction products, both models and polymers, are also reported.

Furthermore, poly(quaternary ammonium salt)s 5 and 6 have been obtained by *N*-alkylation of poly(γ-aminoalcohol)s with methyliodide.

* References 12 and 8 are to be considered Parts 1 and 2 in this series

RESULTS AND DISCUSSION

Scheme 1



†Structures in *Table 2*

Reduction of model compounds

As non-macromolecular model compounds to be reduced, we have chosen the same bis(Mannich base)s used

0032-3861/82/111693-05$03.00

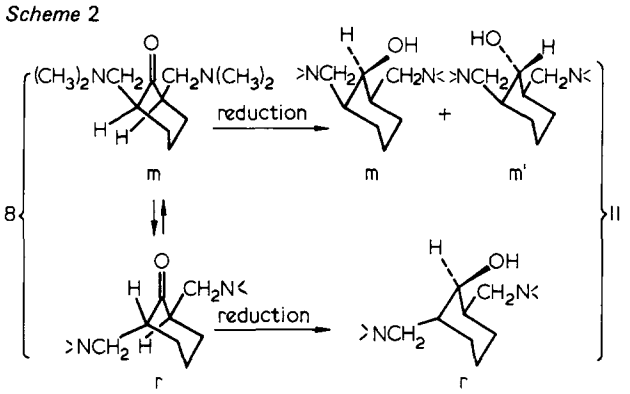
as monomers in the synthesis of poly(β-aminoketone)s, namely 1,5-bis(dimethylamino)pentan-3-one (structure 7), 2,6-bis(dimethylaminomethyl)cyclohexanone (structure 8), *p,p'*-bis(3-dimethylaminopropionyl-1)diphenyl (structure 9) and *p,p'*-bis(3-dimethylaminopropionyl-1)diphenylether (structure 10).

The reduction was performed in two ways, (i) with hydrogen and catalysts, and (ii) with $LiAlH_4$ (see Experimental section). Both methods gave the corresponding γ-aminoalcohols in very good yields.

In principle, stereochemical problems may be encountered in the reduction of bis Mannich bases 8 [10.

The bis Mannich base 8 (*Scheme 2*) was an equilibrium mixture of meso (m) and racemic (r) isomers, containing, at room temperature, 75% of 8m and 25% of 8r. The crystallized dihydrochloride of 8, however, contains 25% of 8m and 75% of 8r[9].

Scheme 2



m = meso form
r = racemic form (only one enantiomer of the racemic pair is represented).

Ketobase	Reduction method	Products (% in the mixture)† IIm	IIm'	IIr
8.dihydrochloride (from ethanol)	catalytic	(25%)	traces	(75%)
↓ OH^-				
8 (free base)	$LiAlH_4$	(6%)	(19%)	(75%)
↓ H_2O, 24 h	catalytic	(75%)	–	(25%)
8 (equilibrated free base)	$LiAlH_4$	(18%)	(57%)	(25%)

†by n.m.r.; within ±5%

The equilibrium point of the free base, once it is obtained from its hydrochloride, is reached after a certain time (some hours to some days at room temperature, according to the solvent).

The $LiAlH_4$ reduction of bis Mannich base 8 gave all the three possible stereoisomers of 2,6-bis(dimethylaminomethyl)cyclohexanol 11, which have been characterized as picrates. Their structures have been determined by ^1H- and ^{13}C-n.m.r. (see *Table 1*). Bis-aminoalcohol 11r, lacking a plane of symmetry, has ten different types of carbon atoms, giving ten signals in its ^{13}C-n.m.r. spectrum. In contrast, both bis-aminoalcohols 11m and 11m' have a plane of symmetry and as a consequence, both have only five non-equivalent carbon atoms, and five signals are present in their ^{13}C-n.m.r. spectra. The structures of 11m and 11m' have been assigned by ^1H-n.m.r., on the basis of the coupling constants relative to the hydrogens in positions 1, 2 and 6.

As far as the relative amounts of the three stereoisomers 11 in the reduction product are concerned, they vary according to the sample of bis Mannich base 8 used. In particular, the $LiAlH_4$ reduction of a sample of 8 just obtained from its hydrochloride, gave 6% 11m, 19% 11m' and 75% 11r, while in the reduction product of an equilibrated sample, the relative amounts of the three stereoisomers were 18, 57 and 25% respectively.

The catalytic reduction of 8 dihydrochloride practically gave only two products 11m (25%) and 11r (75%) with only traces of 11m'. However, the catalytic reduction of an equilibrated sample of the free base 8, gave 75% 11m and 25% 11r. The fact that no 11m' was obtained apparently demonstrates that, in this case, the catalytic reduction is stereospecific. The above results are summarized in *Scheme 2*. The reduction product of bis (Mannich base) 9 with both methods behaves as a single compound. In fact, by using t.l.c. and n.m.r. techniques we failed to obtain evidence of the presence of more than one stereoisomer. The same results apply to the reduction product of the bis Mannich base 10.

Reduction of poly(β-aminoketone)s

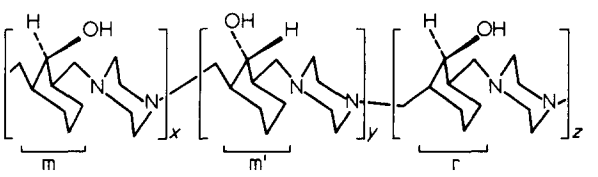
We found that under the conditions we used (see Experimental section) the catalytic reduction of poly(β-aminoketone)s 1a–c and 2a–c invariably stopped after 10–20% of the theoretical amount of hydrogen was consumed. We think that the polymer is strongly adsorbed by the catalyst which is then rapidly deactivated.

However, the same polymers could be quantitatively reduced with $LiAlH_4$. The reductions were performed in refluxing tetrahydrofuran, and proceeded equally well if the starting polymer was insoluble in this medium. In all these cases the reductions were carried out in suspension.

The analytical data of the poly(γ-aminoalcohol)s 3a, 3b, 3c and 4a, 4b, 4c are reported in *Table 2*, together with their intrinsic viscosities and solubility data.

It may be noted that the intrinsic viscosities of the poly(γ-aminoalcohol)s and of the parent poly(β-aminoketone)s were of the same order. This suggests that no extensive degradation occurs during the reduction process.

The stereochemistry of poly(γ-aminoalcohol) 3b was studied by ^{13}C-n.m.r. (see Experimental section). It was found that the three possible configurations of the repeating units are present in a ratio which roughly corresponds to that observed in the product obtained with $LiAlH_4$ reduction of an equilibrated sample of its non-macromolecular model 8. Therefore, to this polymer the following structure may be assigned:



3b

The stability of poly(γ-aminoalcohol)s 3a–c and 4a–c in solution has been determined viscosimetrically. Our results demonstrate that no degradation occurs after standing for several days in protic or aprotic solvents, at 60°C.

Poly(quaternary ammonium salt)s

We have studied the reaction of poly(γ-aminoalcohol)s with methyliodide to the corresponding poly(quaternary ammonium salt)s on polymers 3b and 4a (*Scheme 1*).

Under the conditions we used the reaction went almost to completion in the case of 4a, while in the case of 3b only about 60% of the amino groups reacted. Therefore, the structures of the products (5 and 6) are essentially as depicted in *Scheme 1*.

Unlike the parent poly(γ-aminoalcohol)s, the new quaternary ammonium polymers are soluble either in cold (polymer 5) or warm (polymer 6) water, but insoluble in most organic solvents, including alcohols.

Conclusions

In conclusion, it seems that the reduction of poly(β-aminoketone)s provides an easy synthetic route to a series of new tertiary amino and quaternary ammonium polymers. The parent polymers are, in turn, easily obtained by polycondensation of bis Mannich bases and bisamines. It is possible, in principle, to synthesize by this route, poly(γ-aminoalcohol)s whose repeating units are purposely tailored in order to reproduce chemical structures already known to be pharmacologically active in non-macromolecular compounds, and to test their activity. Such a study is presently in progress.

EXPERIMENTAL

^1H and ^{13}C n.m.r. spectra were run in $CDCl_3$ on C-60 HL Jeol and XL 100 Varian spectrometers respectively (chemical shifts are given in δ ppm, using TMS as internal reference; coupling constants are given in Hz). Intrinsic viscosities were measured in $CHCl_3$ at 30°C with an Ubbelohde viscosimeter, using an automatic timer. Analyses were performed on a FeM mod 185 CHN analyser. Melting points are uncorrected.

Bis Mannich bases 7–10

1,5-Bis(dimethylamino)pentan-3-one 7[10], 2,6-bis(dimethylaminomethyl)cyclohexanone 8[11], *p,p'*-bis(3-dimethylaminopropionyl-1) diphenylether 10[8], were prepared as described in the literature. They were purified according to refs. 8 and 12.

Poly(β-aminoketone)s 1a–c and 2a–c

These polymers were also prepared as described in the literature[8].

Reduction of non-macromolecular models and characterization of the resulting γ-aminoalcohols

Mannich bases 7–10 were reduced either with hydrogen and catalyst (Method A) or with $LiAlH_4$ (Method B). The following synthetic procedures given in the case of bis Mannich base 8 may be applied to all the bis Mannich bases reported here.

Method A. A suspension of the dihydrochloride of 8 (2 g, 0.007 moles) and PtO_2 (0.1 g) in ethanol (20 ml) was hydrogenated in a Parr apparatus at 2.5 kg cm^{-2} and room temperature until no more hydrogen was absorbed. The reaction mixture was filtered, and the filtrate evaporated under reduced pressure. The residue was dissolved in water (20 ml), made alkaline (NaOH) and extracted with ether (5 × 25 ml). The combined ethereal extracts were dried (Na_2SO_4) and evaporated to dryness *in vacuo* yielding 1.9 g (95%) of γ-aminoalcohols (see *Scheme 2*).

Method B. A solution of 8 (7 g, 0.033 moles) in anhydrous ether (20 ml) was added dropwise under cooling to a stirred suspension of $LiAlH_4$ (0.7 g, 0.018 moles) in ether (50 ml). The reaction mixture was refluxed for 1 h, then hydrolysed with water. The precipitated hydroxides were filtered off, and the filtrate was washed with a little water, dried (Na_2SO_4), and evaporated to dryness *in vacuo*. Yield 7 g (98%).

1,5-Dimethylaminopentan-3-ol. Obtained by catalytic hydrogenation (Method A) of the aminoketone 7 is an oil[13]. It was characterized as picrate, M.p. 129°–130°C (from ethylacetate). Analysis: Calculated for $C_{21}H_{28}N_8O_{15}$: C, 39.87; H, 4.46; N, 17.72%. Found: C, 40.8; H, 4.6; N, 16.7%. ^1H n.m.r. of the free base: δ 3.8 (1H, m, H–C–O); 2.5 (4H, m, CH_2–N); 2.3 (12H, s, N–CH_3); 1.6 (4H, m, CH_2–C).

2,6-Bis(dimethylaminomethyl)cyclohexanols 11. Catalytic reduction by Method A of an equilibrated sample (24 h in H_2O at room temperature) of free Mannich base 8, gave a mixture, containing 75% 11m (by n.m.r.), which was isolated and purified as picrate[14]. M.p. 217°–219°C (from 1:1 ethanol/water). Analysis Calculated for $C_{24}H_{32}N_8O_{15}$: C, 42.86; H, 4.79; N, 16.66%. Found: C, 42.3; H, 4.8; N, 16.2%. ^1H n.m.r. of the free base recovered from its picrate: δ 5.2 (1H, s, OH); 3.9 (1H, s, H–C–O); 2.7–2.1 (16H, m, CH–CH_2–NCH_3); 2.0–1.1 (6H, m, $(CH_2)_3$).

$LiAlH_4$ reduction (Method B) of an equilibrated sample of bis Mannich base 8 gave a mixture (see *Scheme 2*), from which 11m' was separated as picrate by fractional crystallizations from ethanol and 1:1 ethanol/water. M. p. 206°208°C (from ethanol/water). Analysis: Found: C, 42.6; H, 4.5; N, 16.5%. ^1H n.m.r. of the free base recovered from its picrate: δ 6.4 (1H, s, OH); 3.2 (1H, t, H–C–O); 2.9–2.1 (16H, m, CH–CH_2–NCH_3); 2.0–0.9 (6H, m, $(CH_2)_3$).

Catalytic hydrogenation of 8 dihydrochloride gave a mixture containing 75% of 11r (by n.m.r.), which was isolated and purified as picrate. M.p. 182°–183°C (from

Table 1 ^1H and ^{13}C n.m.r. data for 2,6-bis(dimethylaminomethyl) cyclohexanols 11

		Aminoalcohol 11		
		11m	11m'	11r
^1H n.m.r.				
H(1)		4.02	3.10	3.60
$J_{H(1)-H(2)}$		<1	9.0	4.5
$J_{H(1)-H(6)}$		<1	9.0	9.0
^{13}C n.m.r.				
C(1)	cyclohexane ring	68.83	80.63	78.26
C(2)	cyclohexane ring	40.33	46.47	35.79
C(3)	cyclohexane ring	25.50	41.23	26.99
C(4)	cyclohexane ring	24.70	28.72	20.00
C(5)	cyclohexane ring	25.50	41.23	28.94
C(6)	cyclohexane ring	40.33	46.47	36.03
$-CH_2-$(2)		62.84	64.75	57.40
$-CH_2-$(6)		62.84	64.75	65.81
$-N(CH_3)_2$(2)		46.02	45.70	45.70
$-N(CH_3)_2$(6)		46.02	45.70	45.77

ethanol). Analysis: Found: C, 42.6; H, 4.5; N, 16.6%. ^{1}H n.m.r. of the free base recovered from its picrate: δ 6.3 (1H, s, OH); 3.6 (1H, dd, H–C–O); 2.9–2.0 (16H, m, CH–CH_2NCH_3); 2.0–0.9 (6H, m, $(CH_2)_3$).

Detailed ^{13}C n.m.r. data for 11m, 11m′ and 11r are reported in *Table 1*.

p,p′-*Bis(3-dimethylamino-1-hydroxypropyl-1)biphenyl.* Obtained by catalytic hydrogenation (Method A) or by $LiAlH_4$ reduction (Method B) of the bis Mannich base 9. It is a crystalline solid, M.p. 173°–174°C (from ethylacetate). Analysis: Calculated for $C_{22}H_{32}N_2O_2$: C, 74.12; H, 9.05; N, 7.86%. Found: C, 74.3; H, 8.5; N, 7.6%. ^{1}H n.m.r.: δ 7.5 (8H, m, ArH); 5.3 (2H, s, OH); 4.9 (2H, t, H–C–O); 2.5 (4H, m, CH_2–N); 2.3 (12H, s, N–CH_3); 1.9 (4H, m, CH_2–C).

p,p′-*Bis(3-dimethylamino-1-hydroxypropyl-1)diphenylether.* Obtained by catalytic hydrogenation (Method A) or by $LiAlH_4$ reduction (Method B) of the bis Mannich base 10. All attempts to obtain crystalline derivatives of this product were unsuccessful. Analysis: Calculated for $C_{22}H_{32}N_2O_3$: C, 70.93; H, 8.66; N, 7.52%. Found: C, 71.7; H, 9.7; N, 7.2%. ^{1}H n.m.r.: δ 7.2 (8H, m, ArH); 6.5 (2H, s, OH); 4.9 (2H, t, H–C–O); 2.5 (4H, m, CH_2–N); 2.3 (12H, s, N–CH_3); 1.9 (4H, m, CH_2–C).

Reduction of poly(β-aminoketone)s

Any attempt to reduce polymers 3a, b, c and 4a, b, c, either as free bases or as hydrochlorides, by catalytic hydrogenation (hydroxylated solvents, press. H_2 2.5 kg cm^{-2}, 10°–30°C, PtO_2 or 10% Pd/C or Ni Raney as catalysts) invariably stopped after 10–20% of the theoretical amount of hydrogen was absorbed. Complete reduction was performed in every case with $LiAlH_4$, according to the following procedure described for the preparation of 3b.

A solution of poly(β-aminoketone) 1b (4.2 g, 0.02 moles) in anhydrous tetrahydrofuran (250 ml) was slowly added dropwise to a stirred suspension of $LiAlH_4$ (0.8 g, 0.02 mol) in tetrahydrofuran. The reaction mixture was refluxed for 1 h, then hydrolysed with water, filtered, and evaporated to dryness *in vacuo*.

The above procedure also applies in the reduction of poly(β-aminoketone)s 1a, 1c, 2b and 2c.

In the case of 2a, a suspension of poly(β-aminoketone) (2.8 g) in tetrahydrofuran (120 ml) and $LiAlH_4$ (0.3 g) was refluxed for 16 h, then worked up as above.

The crude poly(γ-aminoalcohol)s were purified by dissolving in benzene or tetrahydrofuran, and reprecipitating with n-pentane. In all cases, yields were almost quantitative.

^{1}H n.m.r. and i.r. data for all polymers 3a–c and 4a–c were in agreement with the proposed structures. Their analytical data are reported in *Table 2*.

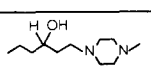
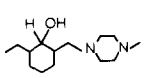
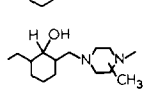
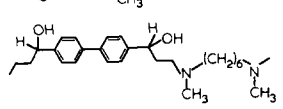
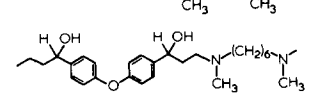
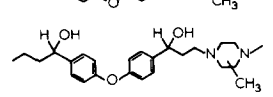
The ^{13}C n.m.r. spectrum of 3b shows 24 peaks, between 80.69 and 20.17 ppm, of which the following ones have been attributed by comparison with the corresponding peaks present in the spectra of non-macromolecular models 11m, 11m′ and 11r (see *Table 1*): δ 71.13, C(1)m; 80.69, C(1)m′; 77.93, C(1)r (intensities ratio m:m′:r = 28:47:25). δ 24.94, C(4)m; 29.01, C(4)m′; 20.17, C(4)r (intensities ratio m:m′:r = 29:53:18). From the above peaks the steric structure of the polymer could be determined (see text).

Poly(quaternary ammonium salt)s 5 and 6

To a solution of poly(γ-aminoalcohol) 3b (3.5 g) in absolute ethanol (50 ml), a large excess of methyl iodide (10 g) was added. The reaction mixture was kept at room temperature for 12 h with occasional stirring. The product precipitated out. It was filtered and washed with absolute ethanol, thus giving poly(quaternary ammonium salt) 5 as white powder, $\eta_{sp/c} = 0.21$ ($c = 1\%$) (in H_2O at 30°C). Analysis: Calculated for 62% conversion: C, 41.24; H, 6.46; N, 7.27; I, 40.88%. Found: C, 41.2; H, 7.1; N, 7.3; I, 40.9%.

The same procedure applies to poly(quaternary am-

Table 2 Poly(γ-aminoalcohol)s by reduction of poly(β-aminoketone)s

System number	Structure of the repeating unit	$[\eta]^a$ dl/g	Analysis[b] C %	H %	N %	Aspect	Solubility[c]
3a		0.27 (0.25)	63.49 63.5	10.66 10.2	16.46 16.1	white powder	K L O (D E M N)
3b		0.12 (0.15)	68.53 68.4	10.54 11.4	13.32 13.2	white powder	E – H, K L N (B J M)
3c		0.12 (0.06)	69.60 70.0	10.78 10.3	12.49 11.8	white powder	B E F G K L (D H J M N)
4a		0.22 (0.23)	76.43 76.9	8.88 9.3	6.86 6.7	white powder	K L (B D E G H M N)
4b		0.12 (0.12)	73.20 72.0	8.98 8.4	6.57 6.4	gum	E K L (B D F G H J M N)
4c		0.17 (0.20)	72.22 71.6	7.91 8.3	7.32 6.8	white powder	E K L M N (H)

[a] In chloroform at 30°C. In parentheses, the values of the parent poly(β-aminoketone)s

[b] Upper row: calculated values; lower row, experimental values

[c] (A) n. Heptane, (B) benzene, (C) ether, (D) dioxane, (E) tetrahydrofuran, (F) methanol, (G) ethanol, (H) n. butanol, (I) acetone, (J) ethylacetate, (K) chloroform, (L) dichloromethane, (M) dimethylsulphoxide, (N) dimethylformamide, (O) water. Letter in parentheses indicates solubility near the boiling point

monium salt) 6 starting from poly(γ-aminoalcohol) 4a (4 g) in n-butanol solution (80 ml), and methyliodide (15 g). The product is a white powder, $\eta_{sp/c}=0.12$ ($c=1\%$) (in H_2O C_2H_5OH 1:1 at 30°C). Analysis: Calculated for 89% conversion: C, 50.32; H, 6.56; N, 4.22; I, 34.04%. Found: C, 50.3; H, 6.7; N, 4.2; I, 34.0%.

ACKNOWLEDGEMENTS

This work has been supported by the 'Progetto finalizzato Chimica fine e secondaria' (grant n. 80,00602,95) of the Italian National Council of Researches (CNR). A helpful contribution by Prof. L. Lunazzi of the Organic Chemistry Department of this Faculty, in running and interpreting the ^{13}C n.m.r. spectra is gratefully acknowledged.

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Effect of crosslinking on the charge storage characteristics of poly(vinyl alcohol)

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(*Received* 25 *February* 1982; *revised* 13 *April* 1982)

The charge storage characteristics of poly(vinyl alcohol) films crosslinked by doping with potassium dichromate and heat treatment have been investigated by surface-charge decay measurement and thermally stimulated depolarization techniques. It has been shown that the mobility of charge carriers decreases with increasing density of crosslinks giving rise to increase in charge storage capacity.

Keywords Polymer; crosslinking; charging; carrier mobility; electrical properties

INTRODUCTION

Recently a number of investigations have been reported on the various properties of poly(vinyl alcohol) (PVA) doped with metallic salts such as $CuCl_2$, $FeCl_3$, $CrCl_3$ etc.[1,2] It is well known that these salts from metal complexes, especially after heat treatment giving rise to crosslinking between the polymeric chains of PVA[3]. The dichromate ion, especially, is responsible for heavy crosslinking in PVA and is used quite extensively in lithographic plates[4]. However, little is known regarding the effect of such complex formation and crosslinking on electrical and charge storage properties. The results of our investigations are reported here.

EXPERIMENTAL

Since the dichromate ion is a good crosslinking agent for PVA, $K_2Cr_2O_7$ (concentration 4% by weight) was used for doping the films. The films were prepared from aqueous solution of PVA (BDH, *MW* 14000) on smooth aluminium substrates or glass slides by solution evaporation technique[5] at 313K. The films were nominally exposed (15 min) to Hg fluorescent lamp (100 lux) and then cured for 30 min at elevated temperatures ranging from 313 to 373K. The surface charge decay characteristics (SCDC) were investigated for the films (50 μ thick) coated on aluminium substrates using a xerographic discharge technique in the same manner as reported earlier[6]. The thermally stimulated discharge currents (*TSD*) were also investigated for these films using samples coated on glass slides with vacuum-deposited silver electrodes on top, forming a surface cell configuration (2.0 $\times$ 0.1 cm^2) and the method for the *TSD* studies was as described elsewhere[7].

RESULTS AND DISCUSSION

Pure PVA films as such accepted very little charge on exposure to corona emission from a wire source held at a potential of 7.0 kV a distance of 2 cm away from the film and it was not possible to record the same. However, films doped with $K_2Cr_2O_7$ accepted a considerable amount of charge and the surface potential was about 200 volts. It was found that this could be further increased to a greater extent by thermal treatment of the samples at elevated temperatures. *Figure 1* shows the typical SCDC observed for doped films cured at various temperatures. Curves 1 to 4 are for the annealing temperatures of 313, 323, 353 and 373K, respectively. It is interesting to note that the surface potential, which is indicative of the amount of charge accepted by the film (V_a), increases by nearly four times when the curing temperature is increased from 313 to

0032-3861/82/111697-03$03.00