

Effect of Alkalies on Suspension Polymerization of Vinyl Acetate Monomer, Properties of Poly(Vinyl Acetate) Beads and Poly(Vinyl Alcohols)

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SYNOPSIS

The use of weak alkalies such as sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3) and their 1 : 1 molar mixture, and strong alkalies such as sodium hydroxide (NaOH) and sodium methoxide (NaOMe) as pH controllers in suspension polymerization of vinyl acetate monomer (VAM) has shown to have diverse effects on the yield of resulting poly(vinyl acetate) (PVAC) beads. Carbon dioxide as such or the carbonate seems to influence the yield. Further, these alkalies have a deep-seated effect not only on properties like viscosity, stereoregularity, glass transition temperature (T_g), and swelling coefficient (Q) of the PVAC beads but also on those of poly(vinyl alcohol) (PVA) obtained by alcoholysis of PVAC beads. The PVAC beads obtained using Na_2CO_3 showed higher viscosity, higher swelling coefficient (Q), and the PVA derived from these beads had higher Q , higher syndiotacticity/isotacticity ratio, and lower T_g .

INTRODUCTION

The effect of solvent on vinyl acetate monomer (VAM) polymerization and microstructure of resulting poly(vinyl alcohol) (PVA) has been extensively investigated.¹ In the suspension polymerization of VAM, sodium bicarbonate (NaHCO_3) has been used as pH controller^{2,3} especially when a hydrophilic initiator like hydrogen peroxide is employed. In continuation of our studies on VAM⁴⁻⁶ and its polymerization^{7,8} with an objective to study the effect of different alkalies on the end properties of the resulting PVAC beads (A-F) and derived PVA (H-L), weak alkalies [e.g., diacidic base, sodium carbonate (Na_2CO_3) (A), 1 : 1 molar mixture of (Na_2CO_3) and NaHCO_3 (B), monoacidic base NaHCO_3 (C & D), and strong monoacidic base such as sodium hydroxide (NaOH) (E) and sodium methoxide (NaOMe) (F)] were chosen as pH controllers for the present investigations.

Though the yield of PVAC beads in weak alkalies (Na_2CO_3 , NaHCO_3 , and 1 : 1 molar mixture) was more than 85%, in NaOH and NaOMe the yields were extremely poor despite using the same molar concentration of alkalies (0.0059 mol, however, in case of Na_2CO_3 , being diacidic base, concentration used was 0.003 mol). Strong alkalies like NaOH and NaOMe hydrolyzed VAM to unstable vinyl alcohol followed by tautomeric rearrangement to acetaldehyde, which inhibited the suspension polymerization and further underwent aldol condensation.^{9,10} Interestingly enough, when carbon dioxide was bubbled in NaOH or NaOMe solutions, the yield improved to more than 80%. The PVAC beads (A) prepared using Na_2CO_3 showed higher viscosity (Brookfield viscometry of molar solution in benzene), low glass transition temperature (T_g), [measured by differential scanning calorimeter (DSC)], and higher crosslinking resulted from chain transfer reaction to polymer, as indicated by swelling coefficient (Q) determined in different solvents (gravimetrically). These bead samples (A-E) were alcoholized using NaOMe under identical conditions to furnish PVA (H-L). While the properties like viscosity (of 4% aqueous solution), T_g , and Q values of the resulting PVA were measured as above, the

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stereoregularity data syndiotacticity, isotacticity, and heterotacticity were derived from IR spectroscopy. The PVA (H) derived from PVAC beads (A) using Na_2CO_3 showed lower T_g (lowest being with NaHCO_3), higher Q values, and higher syndiotacticity to isotacticity ratio. The viscosity, however, was not significantly affected.

EXPERIMENTAL

Material

VAM and acetaldehyde Manufactured by VAM Organic Chemicals Ltd., India was used. PVA, GH-17 manufactured by Denka Poval, Japan, was used. Paraldehyde was prepared¹¹ by acid-catalyzed reaction (using sulfuric acid) on acetaldehyde and purified by fractionation. Hydrogen peroxide (30% aqueous solution) as initiator, Na_2CO_3 , NaHCO_3 , and NaOH obtained from Sarabhai Chemicals, India. NaOMe used was prepared by dissolving sodium in anhydrous methanol under anhydrous conditions and purity checked.¹² Petroleum ether, benzene, methanol, and hexane all of AR grade (E. Merck, India) were used.

Polymerization and Alcoholysis Procedure

PVA (0.4 g) was dissolved in water (500 mL) at 80°C ($\pm 2^\circ\text{C}$) under stirring for 1 h, and the solution was cooled at 40°C in a three-necked round-bottom flask, equipped with a mechanical stirrer, a thermometer, and a reflux condenser. After adding the initiator (H_2O_2 solution, 0.8 mL), the desired alkali

solution (pH 10.5–11, for quantities see Table I) was added such that pH of reaction mass was maintained between 7.5 and 8. Acetaldehyde (0.4 mL), paraldehyde (1.84 mL), and VAM (500 g) were added (in one lot each) resulting in the drop of pH of reaction mixture to 5.5. The temperature of reaction mass was increased to 66°C ($\pm 1^\circ\text{C}$), and the reaction continued till reflux ceased and the reaction temperature increased to 91°C (6 h except in cases of NaOH and NaOMe where temperature were only 67 and 65°C , respectively, even after 25 h). The reaction mass was next cooled to 50°C and diluted with chilled water (500 mL of 10°C). PVAC beads were filtered, washed with water ($150\text{ mL} \times 3$), and dried at ambient temperature to constant weight. The yield of PVAC beads are summarized in Table I.

A modification occurred in the case of NaOH and NaOMe (E1 and F1 Table I) wherein carbon dioxide (22 mL) was passed in alkali solutions (the initial pH of 11 changed to 7.5) prior to the addition in the reaction flask (final pH being 5.5); the beads were obtained in 88 and 95% yield, respectively. PVAC beads (50 g) were dissolved in 200 g methanol and alcoholized using 25 mL of 0.3N NaOMe solution in methanol as reported in the literature.¹⁵ The yield of PVA in all the experiments were between 97 and 98%.

Characterization

The viscosity of PVAC beads (in molar solution in benzene) was determined using a Brookfield viscometer, model LVT, spindle No. 1 and rpm 60. The

Table I Effect on Alkali on Properties of PVAC Beads

PVAC Sample	Alkali Used	Qty. of Alkali (g)	Reaction Time (h)	Yield (%)	Properties of PVAC	
					Viscosity of Molar Soln. at 20°C (± 1 cps)	T_g ($^\circ\text{C}$)
A	Na_2CO_3 NaHCO_3 - Na_2CO_3 mixture (1 : 1)	0.10	6.0	85.8	72.0	46.3
B		0.30	6.0	92.7	32.0	45.4
C	NaHCO_3	0.50	6.0	95.6	20.0	45.0
D ^a	NaHCO_3	0.50	6.0	87.0	28.0	46.0
E	NaOH	0.24	25.0	06.0	46.2	46.8
F	NaOMe	0.32	25.0	No sead formation		—
E1	NaOH + CO_2	0.24	6.0	88.0	13.0	45.6
F1	NaOMe + CO_2	0.32	6.0	95.0	13.0	—

^a 0.6 mL of hydrogen peroxide as initiator was used instead of 0.8 mL.

viscosity of 4% aqueous PVA solution was determined using a Ostwald Fenske viscometer.

Stereoregularity Data

The atacticity of PVAC and PVA were determined by calculating the ratio of absorption bands in IR spectra recorded on a Perkin-Elmer IR spectrophotometer, model 137. T_g were measured by employing DSC, model DuPont 1090 (made in U.S.A.) by employing a heating rate of 10°C/min.

Swelling measurements were carried out by swelling PVAC beads for different intervals at 35°C ($\pm 1^\circ\text{C}$) in petroleum ether, petroleum ether-benzene (95 : 5, V/V), and hexane-benzene (95 : 5, V/V). The PVAC beads (0.2 g) were immersed in 25 mL of the solvent in a stoppered conical flask. The samples were taken out at regular intervals, surface dried by filter paper, and weighed. The process was repeated till equilibrium swelling was obtained. Similarly in PVA samples swelling measurements were carried out gravimetrically in methanol-water (95 : 5, V/V) and benzene.

RESULTS AND DISCUSSION

The role of alkali in suspension polymerization of VAM leading to PVAC beads had been essentially as a pH controller. The effect of five different alkalies (pure or in combination) has been studied (Table I) under identical experimental conditions (except in case of D where low initiator concentration was used). It is indeed interesting to note that with weak alkalies like Na_2CO_3 , NaHCO_3 , or (1 : 1) combination the PVAC beads were obtained in high yield (85.5–95.6%), whereas in the case of strong alkalies such as NaOH or NaOMe despite using same alkali concentration in terms of their acid equivalence, as depicted in cases E and F (Table I), the yields were only 6 and 0%, respectively. Suspension polymerization in the presence of strong alkalies like NaOH and NaOMe VAM is hydrolyzed to unstable vinyl alcohol, which rearranged immediately to tautomeric acetaldehyde (the tautomeric ratio vinyl alcohol-acetaldehyde is 1 : 30000). Acetaldehyde inhibited the suspension polymerisation of VAM. Furthermore, it underwent on aldol condensation in the presence of strong alkalies yielding resinlike oil.¹⁰ Thus the role of carbon dioxide, which is possibly being generated during the neutralization of Na_2CO_3 or NaHCO_3 with acetic acid (present in VAM in ppm levels), is not clear. From the results obtained, it seems that its presence affected significantly the

yield of PVAC beads. The evolution of carbon dioxide suppressed the hydrolysis of VAM to vinyl alcohol and thus the formation of acetaldehyde. This is further confirmed by experiments (E1 and F1 in Table I) wherein bubbling of carbon dioxide in the aqueous solution of NaOH and methanolic solution of NaOMe, prior to their addition to the reaction system, resulted in enormous improvement in the yield of the beads. Since these cases (E and F) were not of industrial interest to us, they were not further studied.

Further, these alkalies have profound effect both on PVAC beads (A–E) and PVA (H–L) obtained by alcoholysis of the PVAC beads, in terms of their viscosity, stereoregularity, T_g , and Q values as discussed below.

On Viscosity of PVAC Beads on PVA

The viscosities of molar solution of A, B, C, D, and E in benzene are given in Table I. The viscosity of sample A was the highest (72 ± 1 cps) and the rest followed the order $E > B > D > C$. The viscosity of D was more, essentially due to lower initiator concentration used in this experiment. The higher viscosity of A supports the probability of branching in PVAC during the polymerization step. The branched polymer formation occurred by chain transfer of polymer predominantly on the acetate methyl group in preference to the backbone: An estimate of the magnitude of the predominance is 40-fold.¹³ At the same time a small amount of branching occurred at the polymer backbone.¹⁴ These beads (A–E) were alcoholized to corresponding PVA (H–L) under conditions illustrated in the experimental section.¹⁵ It was noteworthy that the viscosity in case of PVA (H) is slightly higher (14.5) because of more branching in the main chain owing to the impeding acetaldehyde formation, which otherwise acted as chain transfer agent. Moreover, carbon dioxide was also evolved by the reaction of Na_2CO_3 and acetic acid present in VAM as discussed. If compared to other PVA samples (I, J, and L) where the viscosity ranged between 13.0 and 13.5 cps. The higher viscosity in case of K (17.0 cps) is quite understandable as for the preparation of its precursor (D); the lower initiator concentration has been used.

This viscosity pattern can be rationalized in terms of at least partial removal of the original branches in PVA, which were originated during the beads formation by the self-grafting tendencies of VAM.¹⁶ It has been well established by several investigators^{17,18} that the branching occurs by the chain transfer re-

action of VAM to polymer at the methyl group of acetate moiety as discussed earlier.

On Stereoregularity of PVAC Beads and PVA

It is well known¹⁹ that the infrared spectrum of PVAC exhibits changes with tacticity. The band at 1125 cm^{-1} corresponds to the conventional atactic PVAC. This band becomes weaker with decreases of syndiotactic structure and a new band appears at 1090 cm^{-1} . Apparently these two bands are associated with the syndiotactic and isotactic structure of the polymer, respectively. The infrared spectra of PVAC beads (A-E) have been recorded quantitatively, but the bands are not well distinguished.

In case of PVA (H-L) the bands at 916 and 850 cm^{-1} are very clear (Fig. 1), which have been used as a pointer of syndiotacticity, isotacticity, and heterotacticity.²⁰ Furthermore, the band at 1146 cm^{-1} has been used as a measure of crystallinity. The band at 916 cm^{-1} has been related to syndiotactic structure of PVA by deduction from spectra of PVA samples (H-L) in our studies.

The data of stereoregularity of PVA are summarized in Table II. The syndiotacticity and isotacticity are much more influenced by different alkalies used during the beads formation step, while the heterotacticity varies only by $+1.3\%$ in all cases. The

order of percent syndiotacticity and isotacticity is as follows:

$$\% \text{ Syndiotacticity} \quad \text{H} > \text{L} > \text{J} > \text{I} > \text{K}$$

$$\% \text{ Isotacticity} \quad \text{K} > \text{I} > \text{J} > \text{L} > \text{H}$$

The ratio of syndiotacticity to isotacticity in H-L were found to be 0.94, 0.54, 0.54, 0.39, and 0.58, respectively. The stereoregularity data indicated that the crosslinking in PVA (H-L) is not so pronounced as in case of A, B, C, and E beads. The main-chain branching is less than the side-chain branching in PVAC beads. The amount of long-chain branching in the resulting PVA is therefore small but not nominal.

On Glass Transition Temperature (T_g) of PVAC Beads and PVA

The T_g were measured by DSC and the data on PVAC beads A-D are given in Table I. In all these bead samples the variation in T_g is only $\pm 1^\circ\text{C}$, which indicates that all these PVAC beads have almost similar structure of polymer backbone, and branching of polymer chain is not so pronounced and thus does not have significant effect on T_g values. It implied from the results of T_g summarized in Table II

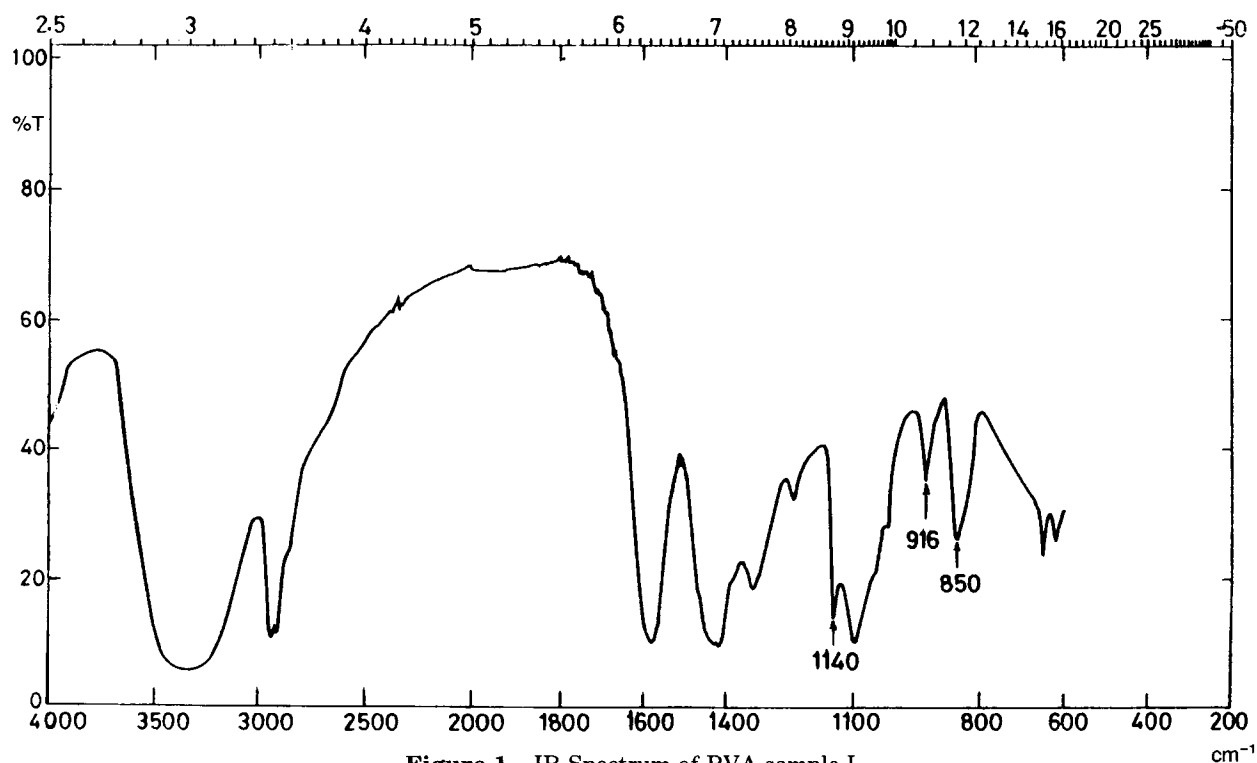


Figure 1 IR Spectrum of PVA sample I.

Table II Effect of Alkali on Properties of PVA, Derived from PVAC Beads by Alcoholysis

PVA Sample ^a	Degree of Hydrolysis (mol %)	Viscosity of Aqueous Soln. at 20°C (± 0.2 cps)	T_g^b (°C)	Stereoregularity			Ratio S/I ^c
				Syndiotacticity (%)	Isotacticity (%)	Heterotacticity (%)	
H	99.0	14.5	65	28.8	30.6	40.6	0.94
I	99.0	13.0	64	21.6	40.0	38.4	0.54
J	99.0	13.0	68	21.7	39.8	38.5	0.54
K	99.7	17.0	—	17.5	45.3	37.2	0.39
L	99.4	13.5	73	22.4	38.9	38.7	0.58

^a PVA samples, H, I, J, K, and L have been correspondingly obtained by alcoholysis of PVAC beads A, B, C, D and E.

^b T_g of PVA powder ranges²¹ between 62 and 80.

^c S refers to syndiotacticity and I to isotacticity.

(variation in T_g values of PVA samples (H-L)] is higher (65–73°C) than in precursor PVAC beads (A–E). Although sample L showed maximum T_g (73°C), in this case the peak is not very sharp as is clear from the plot of heat flow (mW) versus temperature (Fig. 2). The increase in specific heat initiated at 26.5°C and showed a peak maxima at 73°C. Since increase in specific heat of polymer accompanies the molecular motion, the broad peak shows

that sample L is comprising polymer molecules of comparatively different structure. The heat flow versus temperature for the bead (E) from which PVA (L) is derived are compared in Figure 2.

On Swelling of PVAC Beads and PVA

In order to evaluate degree of crosslinking, swelling measurements of PVAC beads (A–E) and PVA (H–

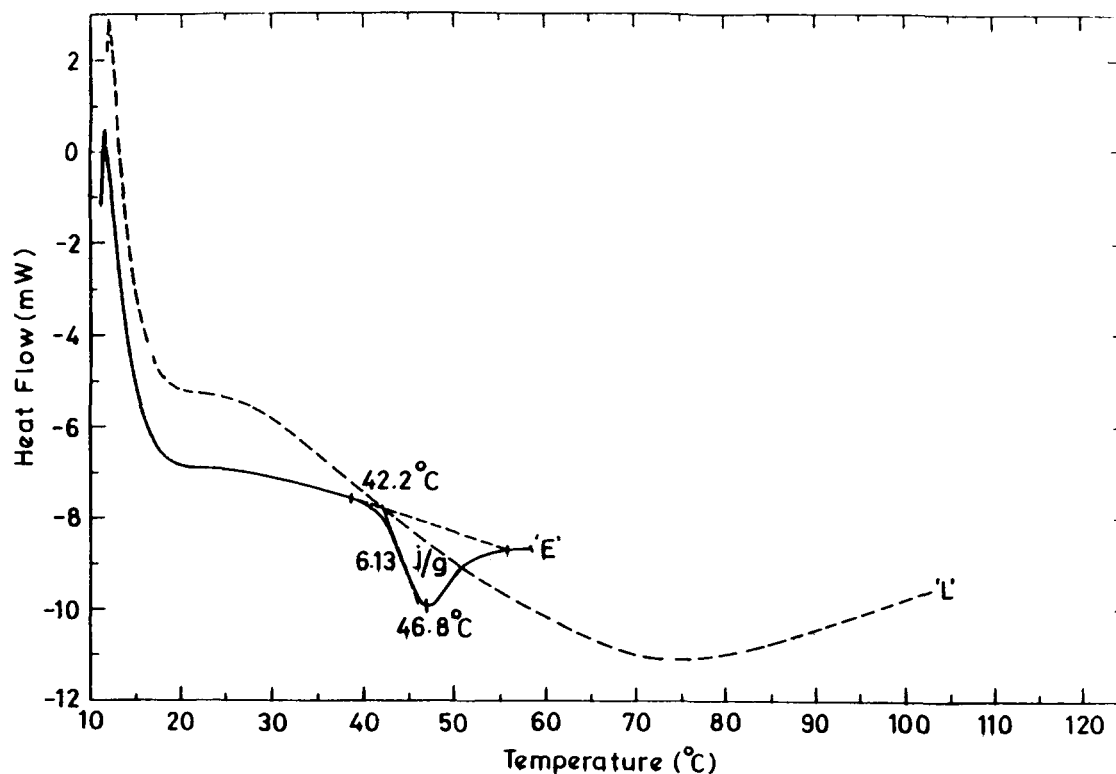


Figure 2 DSC curve of PVAC beads E (—) and PVA (---).

Table III Swelling Measurements of PVAC Beads Using Different Solvents

PVAC Sample	Solvent Used								
	Petroleum-Ether			Petroleum Ether-Benzene			Hexane-Benzene (95 : 5)		
	Time (h)	Sw ^a (%)	Sw ^b (Q)	Time (h)	Sw ^a (%)	Sw ^b (Q)	Time (h)	Sw ^a (%)	Sw ^b (Q)
A	25.0	11.6	0.2412	25.0	29.1	0.4533	25.0	29.1	0.4402
B	25.0	8.8	0.1396	25.0	24.3	0.3781	25.0	24.8	0.3752
C	25.0	2.9	0.0460	25.0	16.7	0.2801	25.0	16.7	0.2526
E	25.0	8.5	0.1349	25.0	23.6	0.3676	25.0	24.4	0.3762

^a Sw refers to swelling.^b Sw refers to swelling coefficient.

L) were conducted. The swelling of PVAC beads and PVA depends to a certain extent on (i) degree of crosslinking of the polymer, (ii) concentration of additives, and (iii) amount of water taken initially during the polymerization.²² Since the last two factors were identical in all respects in these experiments, the only variation was in types of alkalis, which is related with the branching of polymer chain. Hence, it is reasonable to assume that crosslinking in PVAC beads and in the corresponding derived PVA is definitely related to the type of alkali used. The percent swelling and *Q* values of beads A, B, C, and E and of corresponding PVA samples H, I, J, and L have been calculated using the following equation:²³

$$Q = \frac{m - m_0}{m_0} \frac{1}{d} \quad (1)$$

where *Q* is the swelling coefficient, *m* the weight of swollen polymer, *m*₀ the initial weight of polymer prior to swelling, and *d* is the density of the solvent

used. It is well known²⁴ that maximum swelling (or the solubility of polymer) occurs when the solubility of solvent (δ_s) and polymer (δ_p) are similar. The swelling measurement data of A, B, C, and E and of PVA and H, I, J, and L are given in Tables III and IV, respectively, and swelling pattern in case of beads is given in Figure 3. It is obvious from Table III that the bead sample (A) has the maximum *Q* value (0.4533) in petroleum ether-benzene (95 : 5). The same trend was revealed in other solvent systems like petroleum ether and hexane-benzene (95 : 5) (Table III). This again supported that crosslinking is more pronounced in A compared to any other bead sample, i.e., B, C, or E, owing to the chain transfer to polymer as discussed earlier. Similarly, based on the *Q* values of B and E, it can be concluded that these samples have almost the same degree of crosslinking, while the sample C is relatively more linear.

A similar trend is observed in the *Q* values of PVA samples, derived from PVAC beads (Table IV); sample H derived from precursor A has the highest

Table IV Swelling Measurements of PVA, Derived from PVAC Beads by Alcoholysis

PVAC Sample	Solvent Used					
	Methanol-Water (95 : 5)			Benzene		
	Time (h)	Swelling (%)	Swelling Coefficient	Time (h)	Swelling (%)	Swelling Coefficient
H	25.0	160.0	2.0160	25.0	210.0	2.4160
I	25.0	157.7	1.9783	25.0	208.0	2.3930
J	25.0	153.0	1.9380	25.0	194.0	2.3319
L	25.0	115.0	1.4490	25.0	124.3	1.4300

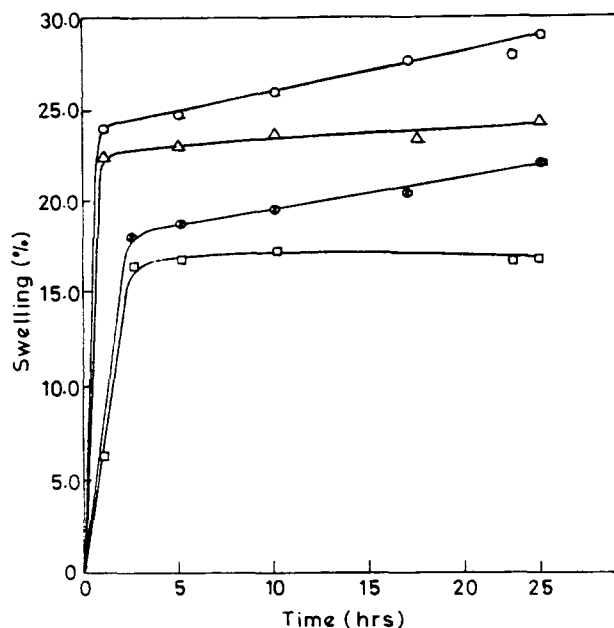


Figure 3 Swelling (%) vs. time in PVAC beads.

Q value in all the solvents tried. PVAC branched polymer (A) when alcoholized gave rise to branched PVA as implied from the results of the crosslinking studies.

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