

Iodination of Plasticized Poly(Vinyl Chloride) in Aqueous Media via Phase Transfer Catalysis

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ABSTRACT: Nucleophilic substitution of chlorine on plasticized poly(vinyl chloride) (PVC) was carried out using potassium iodide (KI) in the presence of a phase transfer catalyst (PTC) in aqueous media. Iodination was confirmed using energy dispersive X-ray analysis (EDAX). The extent of iodination was studied with respect to time, temperature, concentration of the reactants, as well as different PTCs. Among the different PTCs examined, tetrabutylammonium bromide (TBAB) and tetrabutylammonium hydrogen sulfate (TBAH) were found to be highly efficient for the reaction. About 25% increase in weight was observed for PVC sheets iodinated under optimal reaction conditions. The thermal stability of the modified PVC was found to be impaired upon iodination. The iodinated PVC released iodide ions when kept in distilled water, as evidenced by UV spectroscopy. Sustained release of iodide ion in distilled water was followed up for about 30 days. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 493–499, 2002; DOI 10.1002/app.10176

Key words: poly(vinyl chloride); phase transfer catalysis

INTRODUCTION

Iodine is rarely found in polymer molecules due to its weak bonding with carbon. Iodine-containing polymers are of interest in the biomedical area because of certain properties such as radiopacity and antimicrobial action associated with the iodine atom. There have been many attempts reported in the literature to prepare iodine-containing polymers. Thus, synthesis and polymerization of iodine-containing monomers have been carried out to impart radiopacity to polymers intended for biomedical use.^{1–4} Plasma polymerization tech-

niques have been employed for preparing iodine containing polymers as candidate resists materials possessing high resistance to oxygen plasma etching.^{5,6} Iodine can form complexes with a variety of polar polymers like poly(vinyl alcohol), poly(vinyl acetate), nylon, poly(vinyl pyrrolidone) (PVP), etc.^{7–10} Iodine is a well-known antiinfectant and counterirritant. Elemental iodine, incorporated into various polymers, has been widely used for antibacterial polymers.^{10,11} Attempts were also made to coat iodine-complexing polymers like PVP onto a polymer surface to impart antibacterial properties.¹² All these involve the release of polyiodide ions into the medium, which then act as the antibacterial agent. Lin et al.¹³ reported on the antibacterial property of iodine covalently bound to polystyrene matrix, and suggested that the antibacterial property is highly dependent on the structure of the iodine containing group in the polymer.

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Chemical modification of PVC has been extensively studied due to the labile nature of the chlorine atoms present in the polymer. Substitution of chlorine atoms of PVC resin by functional groups such as dithiocarbamate, thioleate, xanthate, dithiophosphate, azide, thiophenoxide, etc., were carried out in aprotic solvents such as dimethyl formamide (DMF) and hexamethylene phosphor-triamide.^{14–16} Phase transfer catalysts (PTC) provides an elegant and efficient way of facilitating reaction between components present in two immiscible phases.¹⁷ In aqueous media, nucleophilic substitution of chlorine atoms on PVC takes place in the presence of a suitable PTC.^{18,19} Nucleophiles such as azide,²⁰ dithiocarbamate,^{21,22} and sulfide²³ can be effectively transferred from an aqueous phase to solid PVC in the presence of a suitable PTC. Here, we attempt to displace some of the chlorine atoms of PVC by iodide ions in aqueous media in the presence of a PTC. PVC finds many biomedical applications such as endotracheal tubes, catheters, containers for the storage of blood and blood products, etc. Controlled iodination of PVC could possibly impart antibacterial properties to the polymer and also make it radiopaque in nature, which would be advantageous in certain biomedical applications.

EXPERIMENTAL

Materials

Medical grade plasticized PVC sheet having a thickness of approximately 0.4 mm was obtained as a gift from Hindustan Latex Ltd., Trivandrum, India. Potassium iodide and phase transfer catalysts like tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), tetrabutylammonium hydrogen sulfate (TBAH), Benzyltriethylammonium chloride (BTAC), and hexadecyltrimethylammonium chloride (HDAC) were procured from Spectrochem Ltd., Bombay, India. Cetyl pyridinium chloride (CPC) was obtained from CDH Ltd., Bombay, India, and 18-crown-6 was from Sigma Chemical Co., St. Louis, MO. All other reagents and solvents were of analytical or equivalent grade.

Methods

Iodination of Plasticized PVC

The reaction was carried out as follows. PVC sheets ($\sim 1.5 \times 2.5$ cm) were treated with potas-

sium iodide ($1\text{--}11 \text{ mol} \cdot \text{dm}^{-3}$) in the presence of different PTCs ($0.01\text{--}0.2 \text{ mol} \cdot \text{dm}^{-3}$) in 10 ml distilled water at 80°C for various time periods (1–24 h) with occasional shaking. After the reaction, the specimens were thoroughly washed with running tap water followed by distilled water and dried in an air oven at about 70°C to constant weight. EDAX was performed on the sheets using X-ray spectrometer (Oxford Instruments, England). Thermal analysis of the modified PVC was carried out using a thermal analyzer (TA Instruments Inc., SDT 2960, USA) at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere. Iodide release from modified PVC was studied by incubating the specimens in 250 mL of distilled water at room temperature (27°C) and determining the percentage change in weight of the specimens with respect to time using an analytical balance. Detection of iodine in the release medium was performed using UV-visible spectrophotometer (HP-8453 Diode-Array, Germany). The UV-Vis spectra of dilute solutions of KI and mixtures of KI and iodine were also recorded in the same range.

RESULTS AND DISCUSSION

Nucleophilic substitution of iodide ions for the chlorine atoms of PVC resin was examined in DMF as well as in a heterogeneous manner in water in the presence of a PTC. In both cases, substitution was taking place as evidenced by the increase in weight of the resin and pronounced color changes that accompanied the substitution reaction. However, after about 10% substitution, the resin was found to be insoluble in all solvents for PVC, and hence, could not be processed. Therefore, attempts were directed towards substitution of the surface chlorine atoms of plasticized PVC in water in the presence of a PTC. Iodinated flexible PVC can find many applications as a biomaterial. Incorporation of a large dense atom like iodine on the surface can impart radiopacity to the material as well as impart some bactericidal property to the material since iodine is known to be a powerful antibacterial agent. Because the substitution is largely confined to the surface, other physical properties of the material may not be compromised to a significant extent.

Figure 1 shows the EDAX spectrum of plasticized PVC sheet reacted with KI for 5 h in the presence of two different catalysts; TBAH (a) and TBAB (b). The spectrum gives a qualitative idea of the different atoms present on the surface of

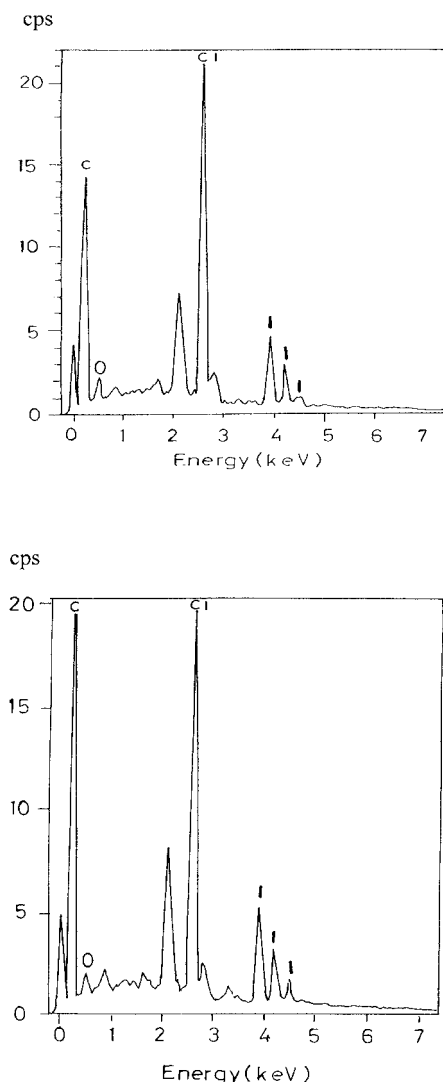


Figure 1 EDAX spectra of plasticized PVC sheet reacted with KI at 80°C for 5 h in the presence of TBAH (a) and TBAB (b). [TBAH] and [TBAB] = 0.15 mol · dm⁻³, [KI] = 6.0 mol · dm⁻³.

the sheet. The peak at 4 KeV is attributed to the L- α signal of iodine. The spectrum also shows the peaks of carbon, chlorine, and oxygen of plasticized PVC, the oxygen peak being attributed to originating from the plasticizer molecule di-(2-ethylhexyl) phthalate (DEHP) present in the material. The absence of any signal due to potassium clearly demonstrates that iodine is not entrapped in the sheet as KI, because the catalyst transfers only the iodide ions from the aqueous phase onto the solid PVC surface. The spectrum of the sheet reacted in the presence of TBAB [Fig. 1(b)] has almost the same appearance as that reacted with KI in the presence of TBAH [Fig. 1(a)], but the

iodine peak shows increased intensity pointing to a higher amount of iodine on the surface. This observation was corroborated by the increase in weight observed for sheets reacted in the presence of these two catalysts. Under identical conditions, reaction in the presence of TBAH showed an increase in weight of 22%, whereas in the presence of TBAB, the increase in weight was 28%. Thus, EDAX spectrum clearly shows the presence of iodine atoms on the surface of the modified PVC sheet.

The reaction conditions for iodine incorporation have been standardized by noting the increase in weight of the specimen as an indication of the extent of iodination. Figure 2 shows the increase in weight of plasticized PVC sheet reacted with various concentrations of potassium iodide in the presence of 0.15 mol · dm⁻³ of TBAB, at 80°C for 5 h. As can be seen, as the concentration of KI is increased, the percentage weight of the sheet also increased, reaching a maximum at about 6 mol · dm⁻³. Subsequent increase in the concentration of KI was not found to result in further increase in the weight of the specimens. Instead, the weight was found to decrease. This trend was found to be similar to that observed earlier in the case of other nucleophilic substitutions carried out on plasticized PVC.^{20,22} The reason for this behavior is presumed to be due to a high degree of association of the nucleophile with the quaternary salt at high concentrations. Quaternary salts are known to associate strongly with large soft anions like I⁻ rather than with small highly hydrated ions like Cl⁻.¹⁷

The effect of different catalysts on the extent of iodine incorporation in plasticized PVC is shown

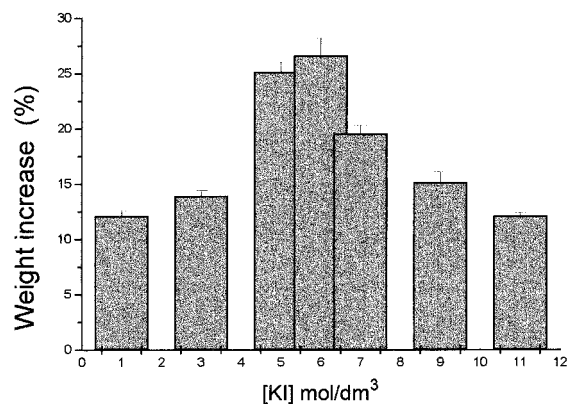


Figure 2 Increase in weight of plasticized PVC reacted with different concentrations of KI with 0.15 mol · dm⁻³ of TBAB at 80°C for 5 h.

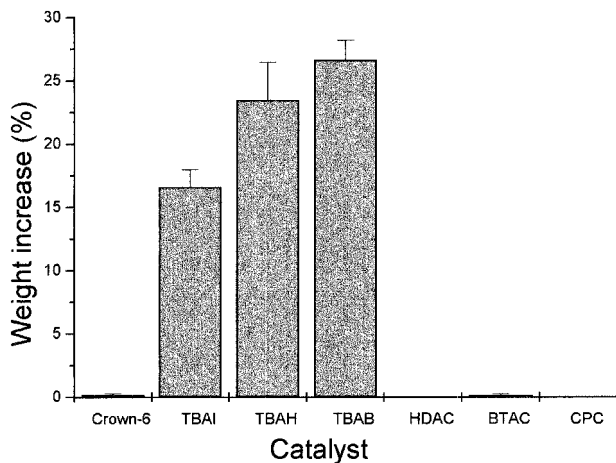


Figure 3 Effect of different PTCs on the iodination of plasticized PVC as observed by the increase in weight of the specimens reacted. $[KI] = 6.0 \text{ mol} \cdot \text{dm}^{-3}$, $T = 80^\circ\text{C}$, time = 5 h.

in Figure 3. Here, PVC sheets were reacted with $6 \text{ mol} \cdot \text{dm}^{-3}$ of KI at 80°C for 5 h in the presence of various PTCs. All tetrabutylammonium salts examined were found to be highly efficient in transporting iodide ions to solid PVC, while 18-Crown-6, HDAC, BTAC, and CPC were found to be virtually inefficient. Similar observations have been noted in the transfer of other nucleophiles onto solid PVC.²² Among the tetrabutyl salts, TBAH and TBAB were found to be almost equally efficient in the transfer process.

The effect of catalyst concentration (TBAB) on the transfer of iodide ions to PVC has been investigated. Figure 4 shows the percentage increase in weight of plasticized PVC sheets reacted with $6 \text{ mol} \cdot \text{dm}^{-3}$ of KI, at 80°C for 5 h in the presence of different concentrations of TBAB. As can be seen, the catalyst concentration required for achieving effective substitution is about $0.15 \text{ mol} \cdot \text{dm}^{-3}$. Concentrations above this were not found to be useful for increasing the substitution reaction. In fact, the extent of iodination seemed to decrease beyond this concentration. Such unusual kinetic behavior has been observed earlier also, and is believed to be due to the aggregation of the quaternary salt with PVC in a bimolecular process, as observed in the case of azide transfer to solid PVC.^{17,20}

Effect of time of reaction on the extent of iodine incorporation onto PVC was also studied (Fig. 5). It can be seen that, as the time of reaction increases, the extent of iodine incorporation increases. When the reaction was carried out for

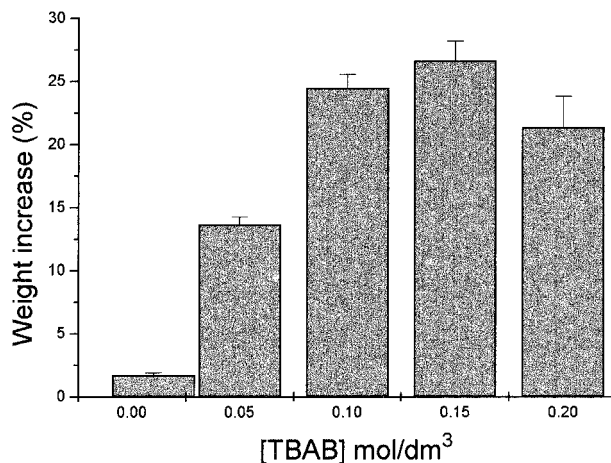


Figure 4 Effect of catalyst concentration on the iodination of plasticized PVC as observed by the increase in weight of the specimens reacted. $[KI] = 6.0 \text{ mol} \cdot \text{dm}^{-3}$, $T = 80^\circ\text{C}$, time = 5 h.

24 h, the percentage increase in weight was found to be about 50% and the color of the sheet became black. The pitch black color developed is presumably due to dehydrochlorination that accompanies the substitution reaction.¹⁴

The effect of temperature on the iodination reaction was examined using TBAB as the catalyst at two different temperatures. Table I shows the percentage weight increase of plasticized PVC sheet reacted with $6 \text{ mol} \cdot \text{dm}^{-3}$ KI in the presence of $0.15 \text{ mol} \cdot \text{dm}^{-3}$ TBAB for 5 h at 70 and 80°C . It can be seen that, as the temperature increases, the extent of iodine incorporation drastically in-

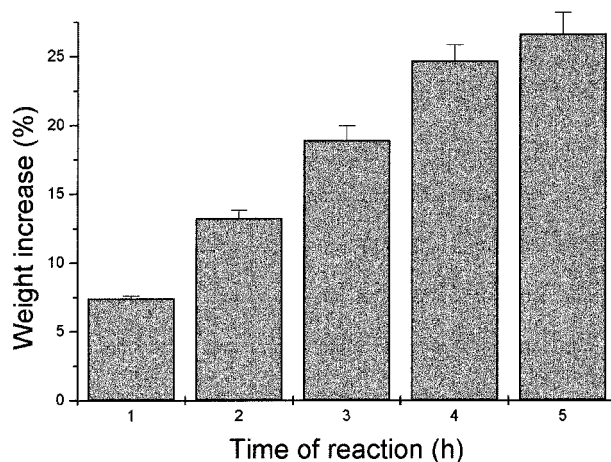


Figure 5 Effect of reaction time on the iodination of plasticized PVC. $[TBAB] = 0.15 \text{ mol} \cdot \text{dm}^{-3}$, $[KI] = 6.0 \text{ mol} \cdot \text{dm}^{-3}$, $T = 80^\circ\text{C}$.

Table I Percentage Increase in Weight of Plasticized PVC Reacted with KI ($6.0 \text{ mol} \cdot \text{dm}^{-3}$) in the Presence of TBAB ($0.15 \text{ mol} \cdot \text{dm}^{-3}$) for 5 h at Different Temperatures

Samples	Weight Increase (%) \pm SD ^a
PVC reacted at 70°C	5.59 ± 0.4
PVC reacted at 80°C	26.60 ± 1.6

^a Average of five determinations \pm SD.

creases. This clearly shows that iodine incorporation onto plasticized PVC will not take place at low temperatures.

Figure 6 shows the thermograms of the unmodified PVC and PVC reacted with $6 \text{ mol} \cdot \text{dm}^{-3}$ KI in the presence of $0.15 \text{ mol} \cdot \text{dm}^{-3}$ TBAB at 80°C for 5 h. The thermogram obtained for unmodified PVC agrees essentially with the literature.²⁴ PVC undergoes endothermic dehydrochlorination in the range of 260–367°C, and further degradation and volatilization start at around 350°C. Also, mixtures of unsaturated carbon-carbon backbone and any unconverted PVC partly char and undergo oxidative degradation to small fragments. The broad endotherm at 260°C and the sharp exotherm at 495°C appear to correspond to these reactions.

When the thermal characteristics of iodinated PVC are compared with those of unmodified PVC, it can be seen that unmodified PVC loses 50% of its weight in the temperature range of 324–327°C, while the iodinated PVC loses that weight at 264–271°C, showing the lower thermal stability of PVC on iodination. When specimens reacted for 24 h were examined for their thermal behavior, similar weight loss was seen at 270–275°C, demonstrating no significant difference between specimens treated for 5 h and 24 h (data not shown). This shift in temperature to the lower values shows a higher rate of endothermic dehydrohalogenation. The thermograms of both iodinated PVCs were found to be almost identical, the only major difference being that the onset of weight loss occurs at 173°C for specimens treated for 24 h, whereas this occurs at 185°C for those treated for 5 h. Thus, the incorporation of iodine onto plasticized PVC impaired the thermal stability of the polymer to a certain extent.

The iodine incorporated PVC was found to lose weight upon incubation in water. The UV spectra of the extract was taken to identify the type of ion present in the solution. Figure 7 shows the UV-Vis spectrum of a dilute solution of KI in water and a solution of iodine and KI in water. It can be clearly seen that, in the case of KI solution, only one peak was found at 280 nm corresponding to

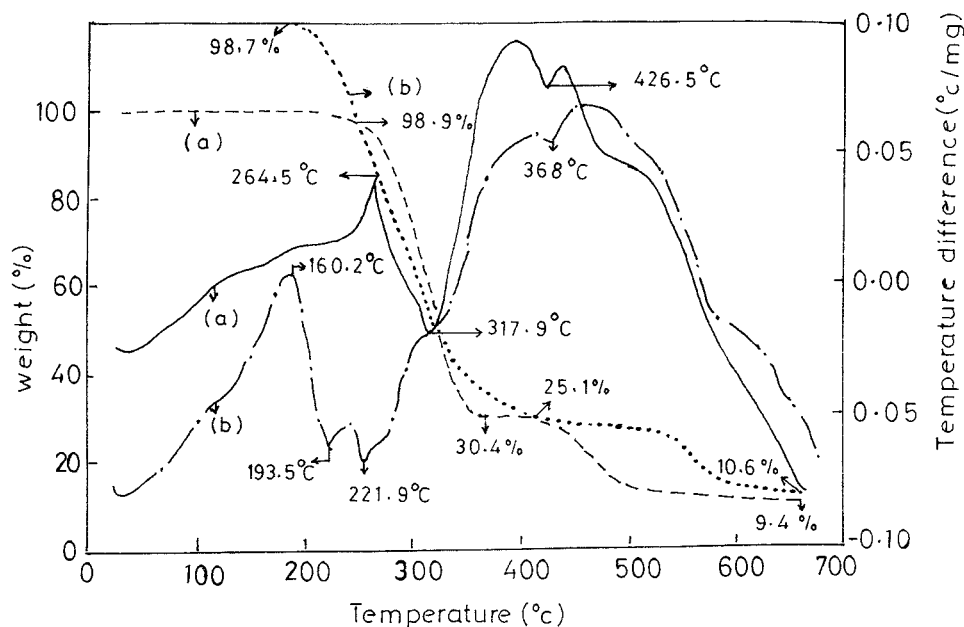


Figure 6 Thermograms of unmodified plasticized PVC (a), plasticized PVC iodinated using $6.0 \text{ mol} \cdot \text{dm}^{-3}$ KI in the presence of $0.15 \text{ mol} \cdot \text{dm}^{-3}$ TBAB at 80°C for 5 h (b).

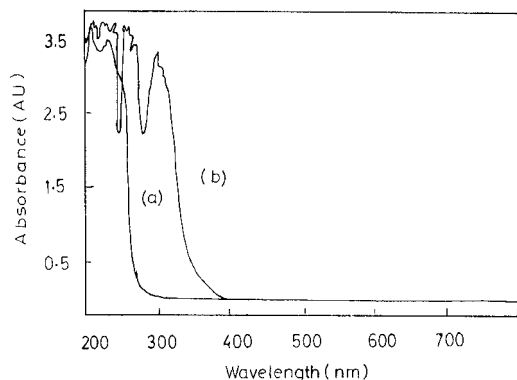


Figure 7 UV-Vis spectra of KI (a) and KI plus iodine in distilled water (b).

iodide ion, whereas in the case of KI–iodine solution three peaks were identified, at 280, 360, and 560 nm, showing the presence of iodide ion and triiodide ions in the solution.²⁵ Figure 8 shows the UV spectrum of extract of iodinated PVC sheet in distilled water. The spectrum shows a single peak at 280 nm similar to that of potassium iodide in solution, clearly showing that the ion that is released from iodinated PVC is iodide ion. The plasticizer DEHP did not enter into complex formation with I^- , as the IR, as well as the UV spectra of DEHP, as well as DEHP reacted with KI under the standardized reaction conditions were found to be identical.

Figure 9 shows the extent of iodide ion released from iodinated PVC sheets over a period of 27 days. The plot shows data for plasticized PVC treated with KI in the presence of TBAB for various periods of time. Specimens treated for 5 h had an initial iodine content of 26.6%, which is reduced to 7.25% after 27 days of incubation in water. The least iodinated specimen (1 h treated)

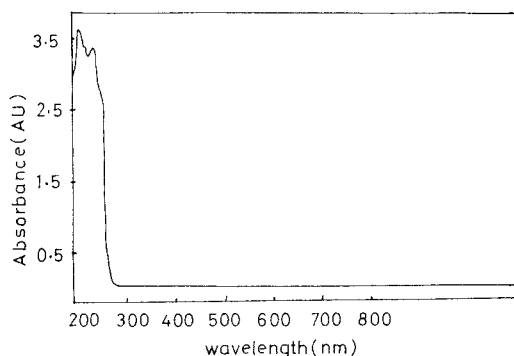


Figure 8 UV-Vis spectrum of 72-h water extract of iodinated PVC.

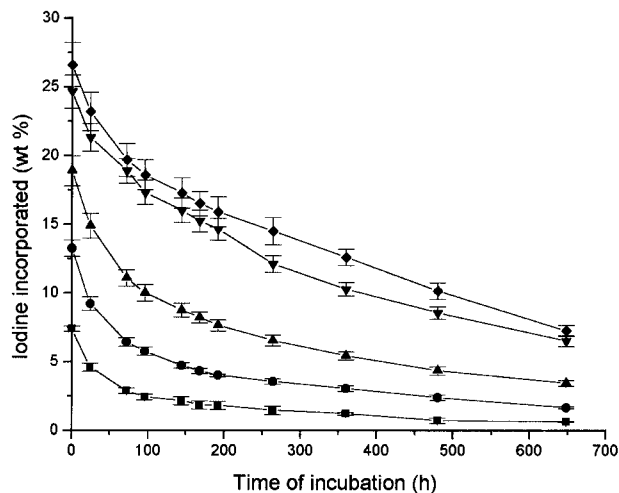


Figure 9 Release of iodide ions into water from iodinated PVC as a function of time: 1 h (■), 2 h (●), 3 h (▲), 4 h (▼), 5 h (◆). [TBAB] = $0.15 \text{ mol} \cdot \text{dm}^{-3}$, [KI] = $6.0 \text{ mol} \cdot \text{dm}^{-3}$, $T = 80^\circ\text{C}$.

had an initial iodine content of 7.38%, which was reduced to 0.63% after 27 days. The amount of iodide ion released into the release medium, even from specimens treated for 2 or 3 h, seems to be significant. The species released from iodinated PVC is undoubtedly I^- , as evidenced by the UV spectra of the extract. The nucleophilic substitution of iodine onto PVC in the presence of a PTC is similar to other nucleophilic substitution reactions on the polymer, and because the bonding of iodine with carbon in polymers is known to be very weak and even plasma generated iodine-containing polymers are known to lose iodine,^{5,6} the very labile nature of the carbon–iodine bond is presumably responsible for the release of iodide ions from the polymer into aqueous media. This observation was also supported by the fact that the release medium progressively became acidic, as shown by pH measurements (pH goes down to about 4), and the polymer also turned brown in color progressively, an indication of dehydroiodination that took place on storage in water.

We have shown earlier that with about 20% iodine in a polymer, the material could be very well imaged radiographically.¹ Thus, in about 3-h reaction, the flexible PVC can contain up to 18% iodine, which would be sufficient to be imaged by X-radiography.

CONCLUSIONS

It is shown that flexible PVC can be iodinated to a very significant extent by a PTC-mediated nu-

cleophilic substitution reaction. However, the bonding of iodine to carbon seems to be weak, as has been reported by previous workers. The labile nature of iodine however facilitates its release as iodide ions into water over extended periods. The iodinated PVC could find use where X-ray opacity and bacterial resistance are desirable in certain biomedical applications. The antibacterial properties of such PVC are being examined, and will be reported elsewhere.

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