Iodine-Incorporated Copolymer of Methyl Methacrylate and *N*-Vinylpyrrolidone. I. Synthesis and Characterization

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IODINE-INCORPORATED COPOLYMER OF METHYL METHACRYLATE AND *N*-VINYLPYRROLIDONE. I. SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Methyl methacrylate and *N*-vinylpyrrolidone were copolymerized in an organic solvent using peroxide initiator and gamma radiation. The copolymers were treated with different weight percentages of molecular iodine in a homogeneous solution of dichloromethane. Iodine was found to be strongly attached to the polymer backbone, and only a negligible amount of free iodine could be extracted from the sample with as high as 40% iodine content. The copolymers of methyl methacrylate and *N*-vinylpyrrolidone prepared under different conditions showed a marked difference in their swelling behavior and thermal stability. The percent swelling and overall thermal stability of the samples decreased after incorporation of iodine into the polymer. The FT-IR, ^{1}H-NMR, thermogravimetric data, and intrinsic viscosity of the copolymers and

their iodine adducts are discussed. The results suggest the presence of specific interactions between the pyrrolidone group and iodine.

INTRODUCTION

A large number of studies involve interaction of polymers with iodine. These polymer–iodine complexes are of considerable interest because of their antimicrobial and disinfecting properties and are widely used in medicine for internal and external purposes.

The most extensively studied iodine–polymer complex is the combination of iodine with polyvinylpyrrolidone (PVP) which was introduced by Shelanski and Shelanski [1]. Molecular and ionic iodine have also been complexed with various copolymers and terpolymers of N-vinylpyrrolidone (NVP) [2, 3]. Kohlhass [4] reported the antimicrobial properties of PVP–I blended with poly(methyl methacrylate). However, detailed studies of the investigation of the structure of such polymer–iodine complexes are not many. The PVP–I complex has been investigated by several groups of researchers but so far there has been no consensus on its molecular structure, particularly on the various forms of iodine that take part in the complexation process. Structures proposed include a helical 1:1 iodine–pyrrolidone complex [5], a pyrrolidone–HI_3–pyrrolidone bridge structure [6], nonspecific (bulk) interaction [7], and others [8, 9]. More information is thus needed in this regard.

Copolymerization of methyl methacrylate (MMA) with NVP and several properties of these copolymers have been studied by many workers. For the copolymerization of NVP with MMA, very low values for the reactivity ratio r_{NVP} have been reported [10]. Huglin and coworkers [10–13] have been engaged in a systematic study of poly(NVP-co-MMA) hydrogels both in chemically and physically crosslinked forms. Other important work includes the characterization of water in MMA/NVP copolymers [14] and studies on the charge-transfer interaction between MMA and NVP by NMR spectroscopy [15].

The present authors, while attempting to prepare an insoluble controlled iodine delivery system for water treatment, did not find a detailed study either on the synthesis or the properties of the MMA/NVP copolymer–iodine complex and its use as a bactericide in water disinfection. A report has been published on the use of a membrane based on MMA and NVP for the ultrafiltration of drinking water [16]. Our aim was to attach iodine to the pyrrolidone group of NVP copolymerized with a hydrophobic monomer in order to prepare a water-insoluble but swellable antimicrobial polymeric system. In this preliminary investigation, the preparation and properties of MMA/NVP copolymers and their iodine adducts were studied. We report the findings from some of these studies in this paper. The antimicrobial properties and release studies of iodine from the iodinated copolymers will be the subject of our subsequent article.

EXPERIMENTAL

Materials

Reagent-grade methyl methacrylate (MMA) and N-vinylpyrrolidone (NVP) monomers (Fluka) were vacuum distilled before use. n-Butyl acetate (E. Merck),

benzoyl peroxide (GSC), resublimed iodine, and dichloromethane (E. Merck) were also reagent-grade chemicals and were used as such.

A ^{60}Co-gamma radiation chamber, supplied by Bhava Atomic Research Center, Bombay, India, was used for the radiation polymerization of samples.

Methods

Synthesis

The copolymerization of MMA and NVP was carried out in a two-necked flask equipped with a nitrogen inlet tube and a reflux condenser. A known amount of benzoyl peroxide in 50 mL n-butyl acetate was taken in the flask so as to have 0.5% initiator concentration with respect to monomer feed (w/w). A fifty-gram monomer mixture (molar ratio MMA:NVP = 1:1) was added to this. The contents were thoroughly mixed and nitrogen gas was bubbled through the solution to provide an inert atmosphere. The solution was then polymerized at 70°C for 3 hours and at 100°C for the next 2 hours. The polymer was precipitated from carbon tetrachloride–petroleum ether and purified twice by reprecipitation from benzene with the same nonsolvent. The polymer (coded CP1) was washed thoroughly with distilled water and dried in a vacuum oven. Yield: 32.7 g. Homopolymers of MMA and NVP were also prepared under similar conditions.

The copolymerization of MMA and NVP was also carried out using gamma radiation. A mixture of 50 g monomers (1:1 molar ratio) and 50 mL n-butyl acetate in an inert atmosphere of nitrogen was irradiated at a dose rate of 30 rad/s for a total dose of 0.32 Mrad at room temperature. The polymer (coded CP2) was precipitated and purified by methods described above. Yield: 14.15 g.

The iodination of the copolymers was accomplished by adding a calculated amount of iodine dissolved in dichloromethane to a known concentration of polymer solution in the same solvent. The weight percentages of iodine varied from 10 to 40. The purple color of the iodine solution changed to dark brown immediately after addition. The uncovered reaction mixture was left in the dark at room temper-

TABLE 1.   Determination of Free Iodine in the Iodinated Copolymeric Films of MMA and NVP

Polymer sample	Total iodine incorporated into the sample (% by wt)	Absorbance at 515 nm	Free iodine in CCl_4, mg/L
I	10	0.012	1.7
II	20	0.013	2.2
III	30	0.016	3.2
IV	40	0.021	4.5
V[a]	20	0.222	4.6

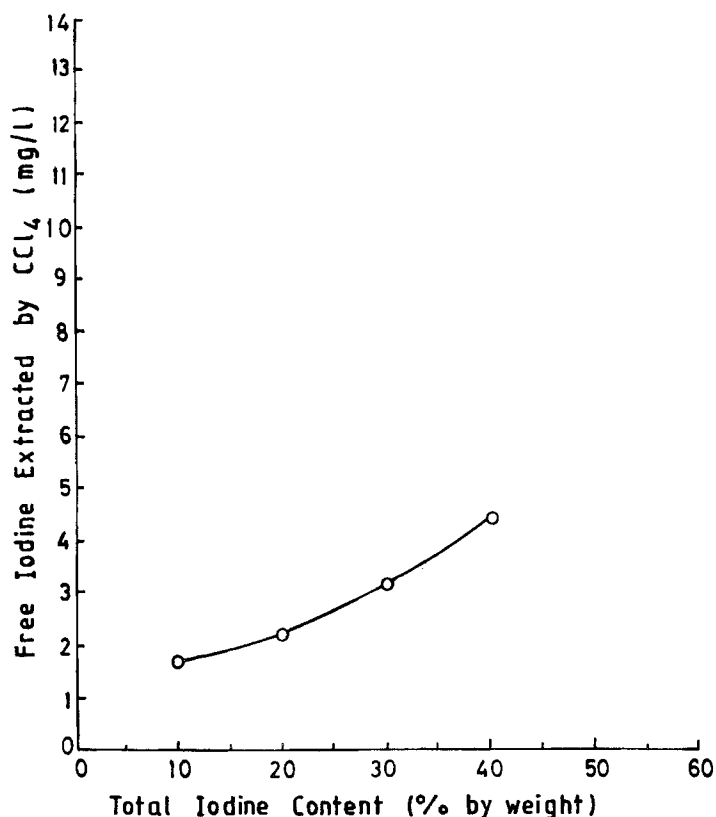[a]Copolymer prepared by gamma radiation.

FIG. 1.   Free iodine concentration in a fixed weight of iodinated copolymers of MMA/NVP containing various weight percentages of iodine.

ature for 6–8 hours. Films of the iodinated copolymers cast on Teflon sheets were thin, transparent, nontacky, and reddish-brown in color; they were also stable to storage.

Determination of Free Iodine Content of the Iodinated Copolymers

A fixed weight of the iodinated copolymers containing various weight percentages of iodine was suspended in 5 mL carbon tetrachloride for 24 hours at room temperature. The absorbance of the suspensions was measured at 515 nm with a UV-VIS Spectrophotometer (Hitachi 100-60), and the free iodine concentration of the iodinated polymers was determined against standard solutions.

Characterization

Solubility

Solubilities of the homopolymers, copolymers, and iodinated copolymers were determined in different polar and nonpolar solvents.

TABLE 2.   Solubility of the Iodinated and Noniodinated
Copolymers in Solvents[a]

| | Sample | | | | |
| | | | | | Iodine adduct of CP1 |
Solvent	CP1	CP2	PVP	PMMA	
Water	sw	sw	s	ns	ns
Methanol	ps	sw	s	ns	ps
Benzyl alcohol	s	s	s	s	ns
DMF	s	s	s	s	s
Dioxane	s	s	ns	s	ns
Acetone	s	s	ns	s	ns
THF	s	s	s	s	ns
Chloroform	s	s	s	s	ns
MEK	s	s	s	s	ns
Ethyl acetate	s	s	ns	s	ns
1,2-Dichloroethane	s	s	s	s	ns
Toluene	ps	ps	ns	s	ns
Hexane	ns	ns	ns	ns	ns

[a]ns = nonsoluble; sw = swollen; ps = partly soluble; s = soluble.

TABLE 3.   Swelling Behavior of Iodinated and Noniodinated
Copolymers

| Time, hours | Percent swelling of | | | | | | |
| | CP1 | CP2 | Iodinated copolymers with various weight percents of iodine | | | | |
			10%[a]	20%[a]	30%[a]	40%[a]	20%[b]
0.5	29.5	2.5	13.0	8.0	3.5	1.2	1.8
1	35.5	3.5	16.7	11.4	5.2	2.4	2.5
2	38.2	5.0	20.0	14.9	7.6	4.0	4.0
4	39.5	6.9	23.1	17.2	10.5	5.8	6.0
6	39.5	8.1	25.0	19.6	13.1	7.5	6.8
8	40.0	9.8	24.7	20.8	13.4	8.8	7.5
24	40.0	10.4	24.3	20.6	13.2	8.9	8.2

[a]Samples prepared from CP1.
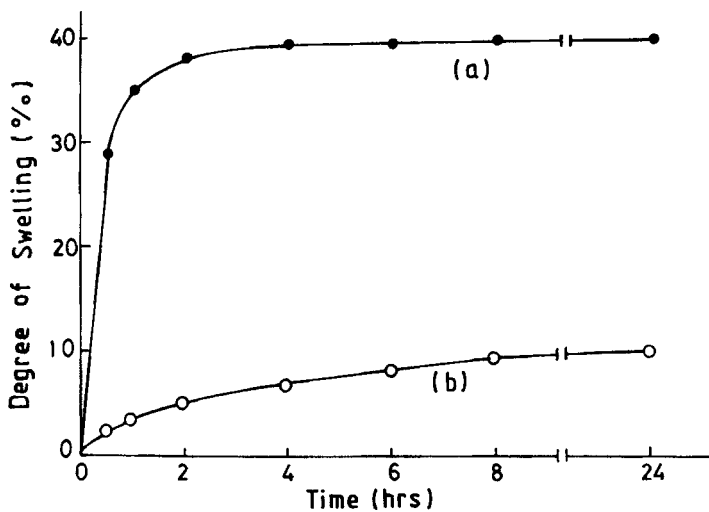[b]Samples prepared from CP2.

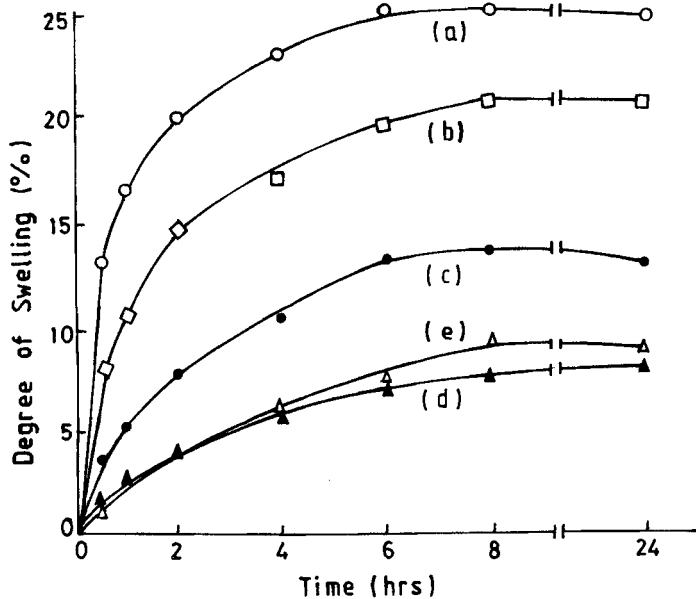FIG. 2.   Degree of swelling of MMA/NVP copolymers. (a) CP1 and (b) CP2.

FIG. 3.   Degree of swelling of iodinated copolymers of MMA/NVP containing various weight percentages of iodine. (a) 10% of CP1, (b) 20% of CP1, (c) 30% of CP1, (d) 40% of CP1, and (e) 20% of CP2.

Swelling Studies

The water uptake capacity of the iodinated and noniodinated copolymer samples was determined by swelling the films in distilled water at room temperature (30 ± 2°C). The weight of the swollen films was determined at various time intervals after blotting out the excess water from the films with filter paper. The percent swelling of the films was then calculated from

$$\% \text{ Swelling} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s and W_d are the weights of the films in the swollen and dry states, respectively.

IR Spectroscopy

The FT-IR spectra of the samples were recorded on a 5 DX Nicolet FT-IR Spectrophotometer using KBr pellets coated with thin films of the polymer samples.

^{1}H-NMR Spectroscopy

^{1}H-NMR spectra of the samples were recorded on a Jeol JNM-FX 100 FT-NMR Spectrometer operating at 99.55 MHz. The spectra were run at room temperature using deuterated solvents with TMS as the reference.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

TGA of various iodinated and noniodinated polymer samples were carried out in a Perkin-Elmer 7 Series Thermal Analyzer in an atmosphere of nitrogen at a heating rate of 10°C/min. DSC scans of the copolymer samples were obtained on a DuPont 9900 instrument from 50 to 350°C at a scanning rate of 10°C/min.

Viscosity Measurements

The viscosity measurements were performed in an AVS 310 Ubbelohde Viscometer (Schott Gerate, Germany) in a constant temperature water bath (30°C). The intrinsic viscosity, $[\eta]$, was obtained by plotting the reduced viscosity of a series of polymer solutions of various concentrations. Extrapolation to zero concentration yielded the intrinsic viscosity.

TABLE 4.   Feed Compositions of Monomers and NVP Content of the Prepared Copolymers

Sample	Feed composition in wt%		NVP content in copolymers by nitrogen analysis, wt%
	MMA	NVP	
CP1	46.27	53.73	56.45
CP2	46.27	53.73	43.92
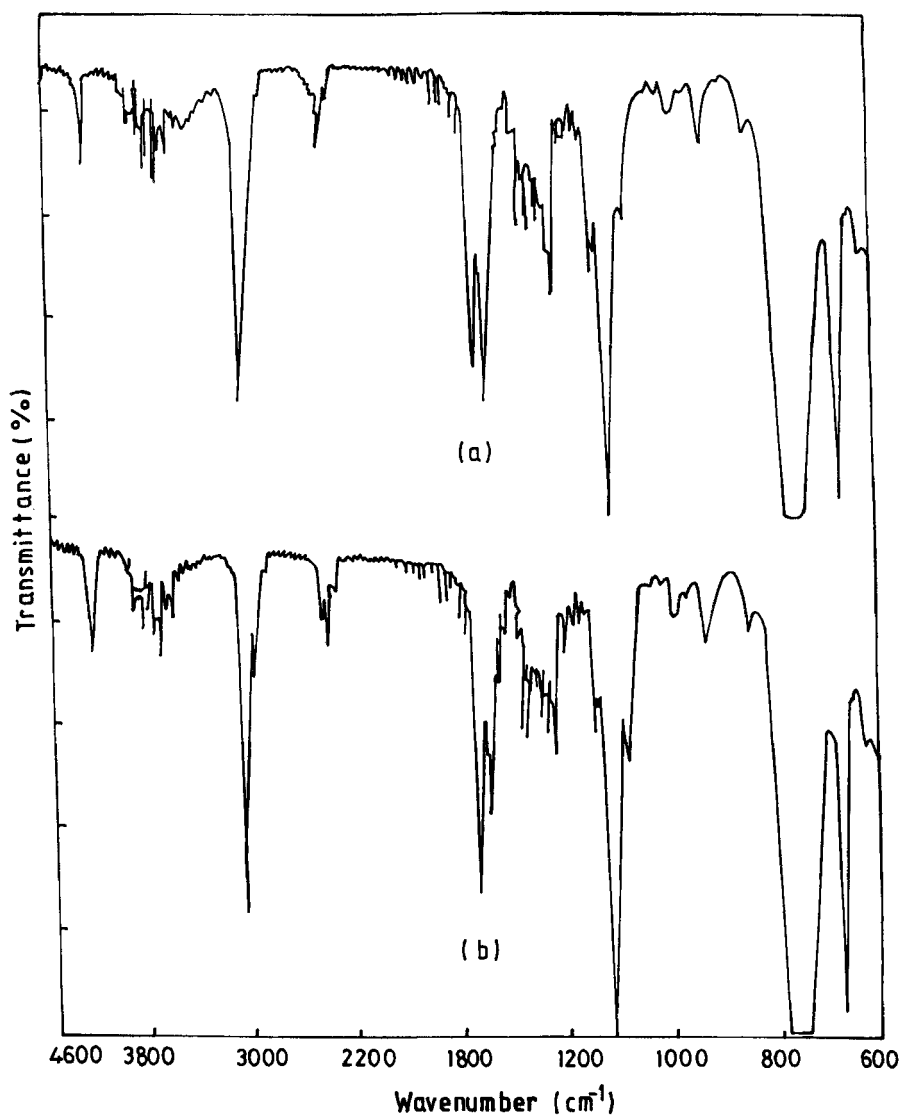
FIG. 4.   FT-IR spectra of (a) CP1 and (b) CP2.

RESULTS AND DISCUSSION

Synthesis

MMA and NVP were copolymerized in *n*-butyl acetate using benzoyl peroxide as well as gamma radiation with 65.4 and 28.0% conversions, respectively. Identification of the reaction product is important as it has been reported [17] that NVP resists polymerization in organic solvents with peroxide catalysts. A very poor yield of the homopolymer, PVP, was obtained when NVP was polymerized in *n*-butyl

FIG. 5.   FT-IR spectrum of MMA/NVP copolymer containing 20% iodine.

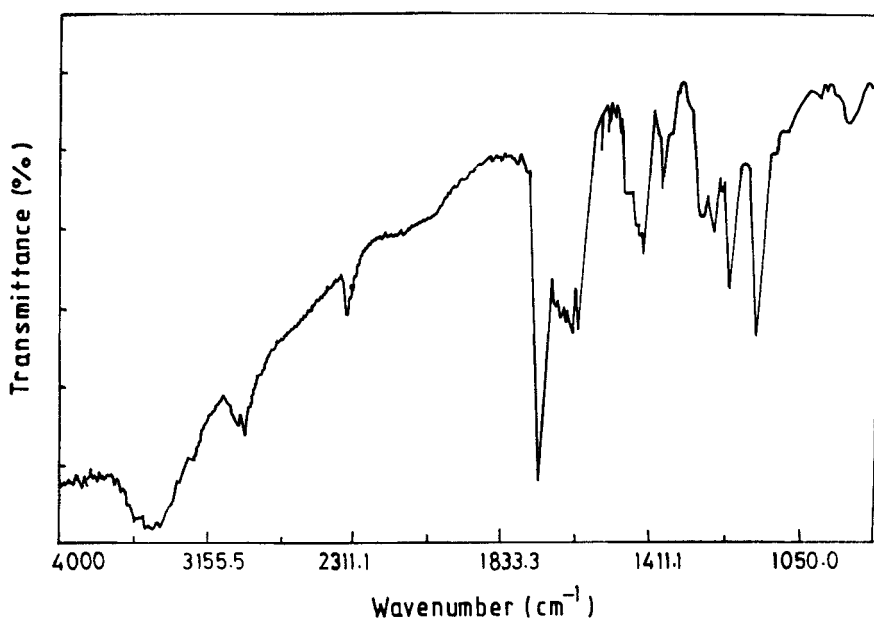acetate using benzoyl peroxide whereas MMA was found to polymerize easily under identical conditions. When NVP (M_1) is copolymerized with MMA (M_2), the reported reactivity ratios of the monomers are $r_1 = 0.05 \pm 0.02$ and $r_2 = 4.4 \pm 1.2$ [10]. Huglin et al. demonstrated that because of this disparity in r values, there is considerable compositional drift during the course of polymerization. Since no attempt has been made by the present authors to suppress the drift in composition during the polymerization reaction, the products were used for characterization as they were obtained.

The attachment of iodine to the copolymers of MMA and NVP was found to be strong enough to reduce the vapor pressure of iodine to almost nil; samples containing as high as 40% iodine (w/w) were stable to storage. Also, a very negligible quantity of iodine was found to be free in the samples when extracted with carbon tetrachloride and measured spectrophotometrically (Table 1 and Fig. 1). The results indicate that almost all the introduced iodine has interacted with the polymer. In fact, PVP ties up with elemental iodine when the two are simply mixed in powdered forms [7]. PVP-I complex has also been prepared in an aqueous solution where iodine has been introduced as the triiodide ion or generated in situ [6, 18]. Although there is general agreement on the stability of the PVP-I complex thus prepared, there is a divergence of opinion regarding the oxidation states of iodine. It has been reported at various times that iodine in the PVP-I complex exists as molecular iodine, iodide (I^-), triiodide (I_3^-), and hypoiodide (IO^-) [6, 7, 19, 20]. The present studies involved the preparation of the polymer–iodine complex in a nonaqueous solvent by incorporating molecular iodine to a copolymer of NVP without any other types of iodine or other ions being present initially. It was ob-
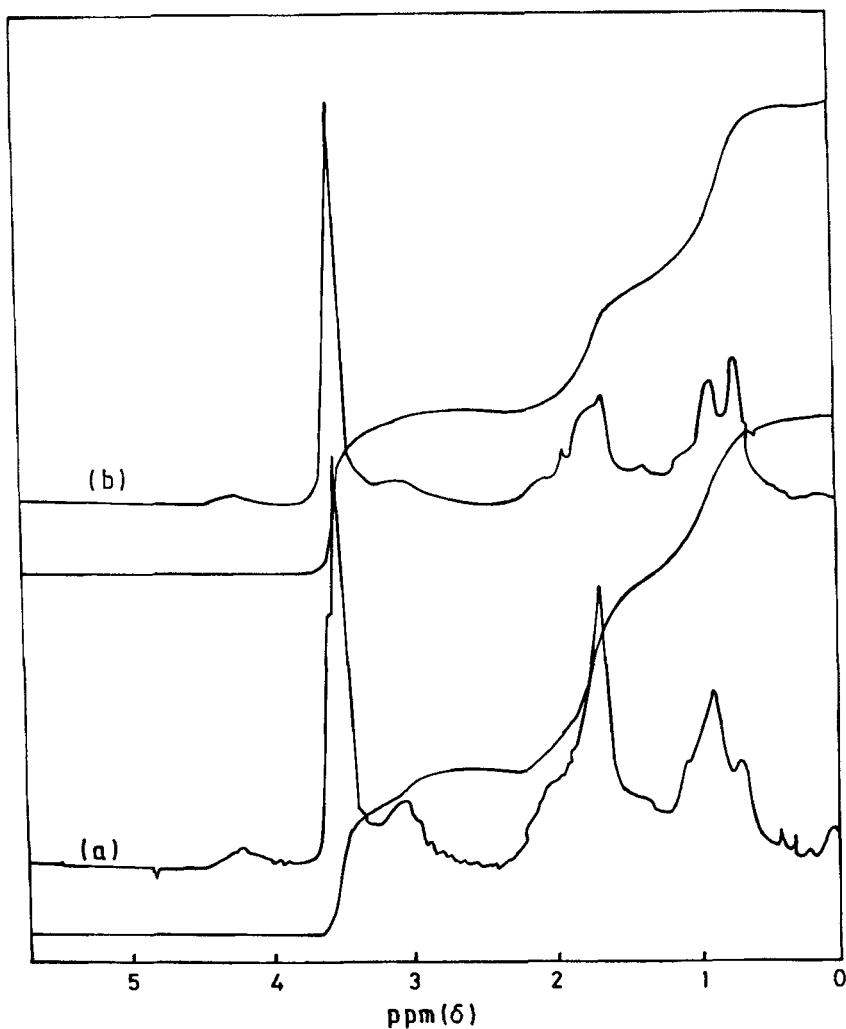
FIG. 6.   ¹H-NMR spectra of (a) CP1 and (b) CP2.

served during the preparation of the iodine adduct that it was stable only when the uncovered reaction mixture of iodine and copolymer solution in dichloromethane was allowed a time period of 6–8 hours. It seems that moisture is probably playing a role in stabilizing the product as suggested by Cournoyer and Siggia [7].

Characterization

Solubility and Swelling Behavior

The solubilities of the homopolymers (PMMA and PVP), the copolymers of MMA and NVP, and the iodine adduct are listed in Table 2. The copolymers are soluble in chloroform, 1,2-dichloroethane, DMF, MEK, benzyl alcohol, acetone,

FIG. 7. ^{1}H-NMR spectra of (a) CP1 containing 20% iodine and (b) CP2 containing 20% iodine.
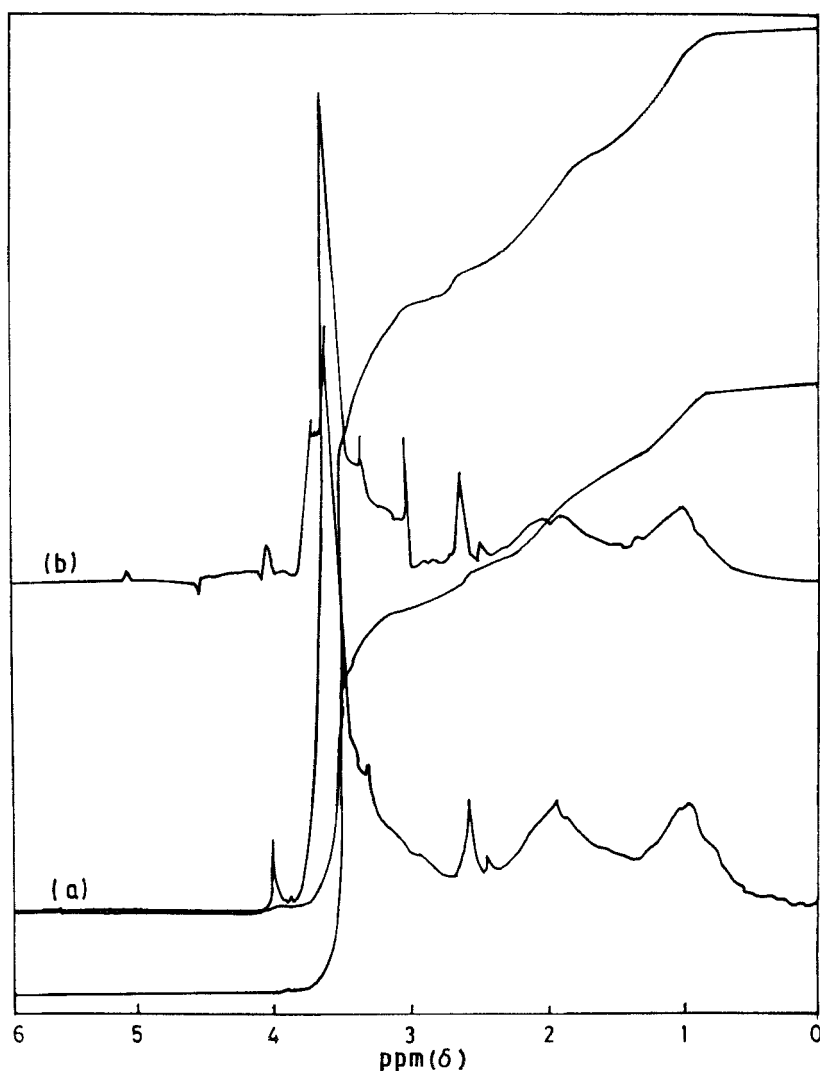
dioxane, THF, and ethyl acetate. On immersion in water, partial solubility was exhibited by none of the samples. The only difference in solubility observed between CP1 and CP2 was that CP2 swelled in methanol while CP1 was partly soluble in it. The results indicate that the samples are linear copolymers. If CP2 is slightly crosslinked by gamma radiation, its solubility has not been affected. Since there is a possibility of the samples being blends, the solubility tests give a rough idea of the polymer composition. That they are insoluble in water but soluble in dioxane (a nonsolvent for PVP) shows that the samples do not have PVP homopolymer. The poor yield of the PVP homopolymer obtained when the monomer was polymerized
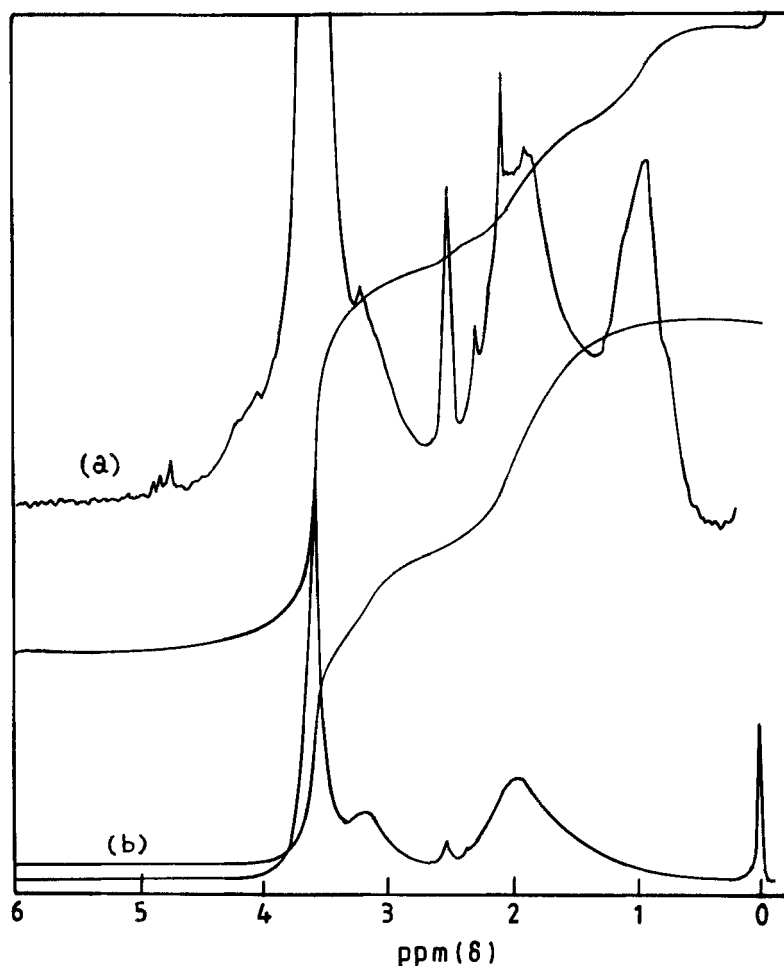
FIG. 8. ^{1}H-NMR spectra of (a) iodinated copolymer of MMA/NVP and (b) commercial PVP-I powder.

in n-butyl acetate demonstrates that NVP resists polymerization under this condition. One of the samples (CP1) is partially soluble in methanol, and the hazy solution becomes clear when a drop of chloroform is added. It is reasonable to assume that the samples are blends of MMA/NVP copolymer and PMMA. CP2 swells in methanol and possibly has a lower content of NVP in the copolymer. The iodine adducts of the copolymers are insoluble in all the solvents except DMSO, DMF, and methanol:chloroform (80:20). This could be due to the polar nature of the iodine complex.

Table 3 presents the percent swelling values for the iodinated and noniodinated copolymer samples. The plots of percent swelling vs time are presented in Figs. 2 and 3. It is evident from the results that there is a great difference in the swelling behavior between the samples prepared under different conditions. The maximum

TABLE 5.   Thermogravimetric Data for PMMA, PVP,
P(MMA-*co*-NVP), and P(MMA-*co*-NVP)·iodine

Sample	NVP content, wt%	Iodine content, wt%	IDT$_1$, °C	IDT$_2$, °C	IPDT, °C	Temperature (°C) at various weight losses			
						20%	40%	60%	80%
PVP	100	—	100	425	412.4	385	458	476	492
CP1	56	—	120	360	425.5	382	418	448	471
CP2	44	—	135	348	402.2	390	412.5	440	445
PMMA	0	—	155	295	358.7	335	360	380	403
CP1	56	20	145	240	410.2	305	412	459	482
CP1	56	30	135	238	388.4	282	380	445	464
CP1	56	40	128	235	374.0	278	342	435	468
CP2	44	20	132	240	400.9	305	410	450	472

degree of swelling observed with the sample polymerized by γ-radiation (CP2) was 10% while that of the sample polymerized by peroxide catalyst (CP1) was 40%. The difference can be ascribed to two factors: 1) since the reactions were run at different temperatures, the samples may have different polymer compositions; 2) CP2 may have a certain degree of crosslinking present in the structure due to gamma radiation. Nitrogen content analysis of the samples supports the fact that CP2 indeed has a lower content of NVP (Table 4).

The percent swelling values of the iodinated samples are lower than those of the noniodinated ones and they decrease with increasing iodine content of the polymer. This can be explained by the fact that there is an increase in the degree of crosslinking of the polymer network caused by iodine. Swell ratios for lightly crosslinked PVP have been noted by Breitenbach [21] who showed that I_2 caused a decrease in swell volume. Iodine has also been used as a crosslinking agent by Bezdek [22] for copolymers of MMA and 2-dimethylaminoethyl methacrylate. The weight of the swollen hydrogel (W_s) would be less due to release of iodine in water with increasing iodine loading of the samples; as a result, the swell ratio of the hydrogels would decrease with increasing iodine content of the polymer.

FT-IR and ^{1}H-NMR Spectroscopy

The FT-IR spectra of the copolymers of MMA and NVP (Fig. 4) show two distinct absorption bands at 1732 and 1682 cm^{-1}, corresponding to the ester carbonyl group unit of MMA and the carbonyl group unit of NVP, respectively, which indicate the presence of both MMA and NVP in copolymers CP1 and CP2. The primary alteration in the IR spectrum of the iodinated copolymer is the disappearance of pyrrolidone ring carbonyl absorption at 1682 cm^{-1} (Fig. 5). Instead, it appears as a weak band at 1646 cm^{-1}. Such a change in the IR spectrum is attributed to the bonding changes in the region of the carbonyl and O=CN groups. Three new absorption peaks are observed at 2017, 1116, and 1055 cm^{-1}. The spectrum, however, shows the ester carbonyl band at 1732 cm^{-1}, thus indicating the noninvolve-
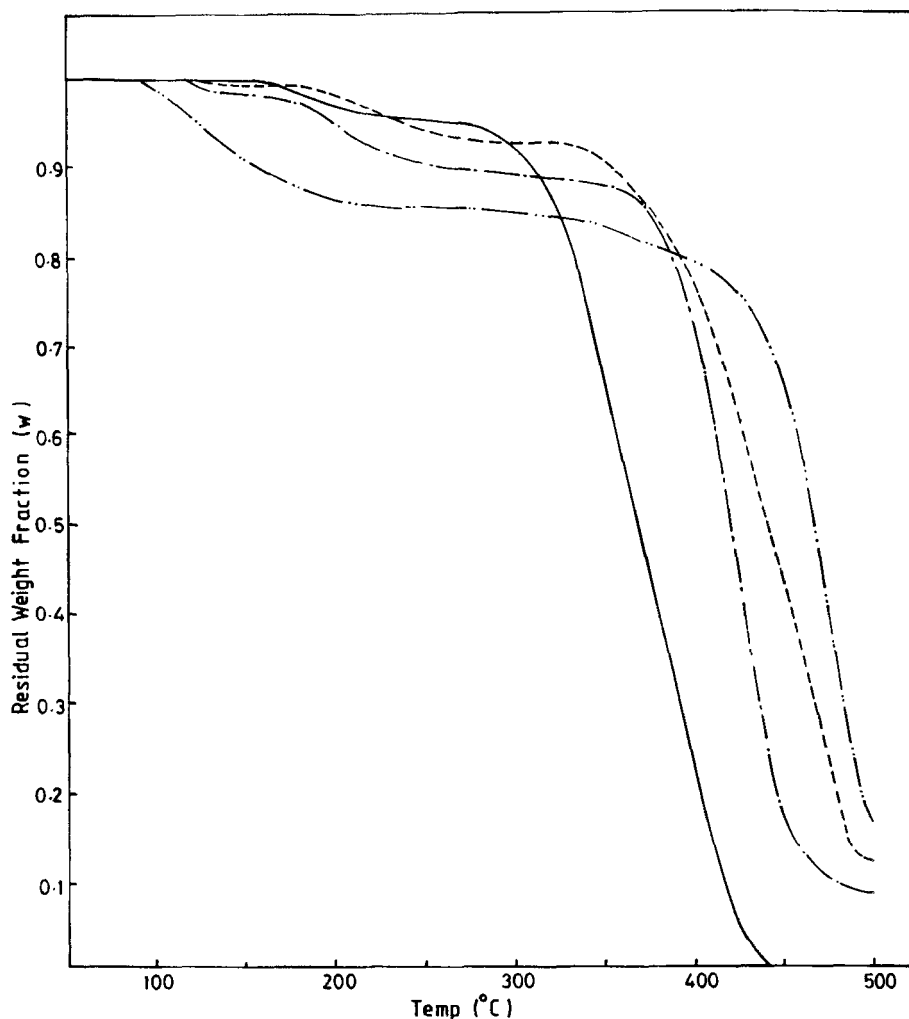
FIG. 9.   TGA curves of homo- and copolymers of MMA and NVP. (——) PMMA,
(— ·· —) PVP, (---) CP1, and (— · —) CP2.

ment of the ester carbonyl group of MMA in the iodination reaction. We suggest
the formation of an unstable molecular complex (MMA/NVP)·I_2 in dichlorometh-
ane as soon as iodine reacts with an NVP unit of the copolymer. Some of it is then
probably reduced by moisture to iodide ion, I^-, with the formation of hydrogen
iodide. We also observed that the aqueous suspension of the copolymer–iodine
complex was acidic in nature. The iodide ion may form polyiodide ion, I_n (n = 3 to
7), with iodine, and this anion may be present in the stable iodine–polymer complex
as suggested by Schenck et al. [6]. However, at this stage it is difficult to predict the
final structure of the stable MMA/PVP–iodine complex.

   ^{1}H-NMR spectra of MMA/NVP copolymers and their iodine complexes are
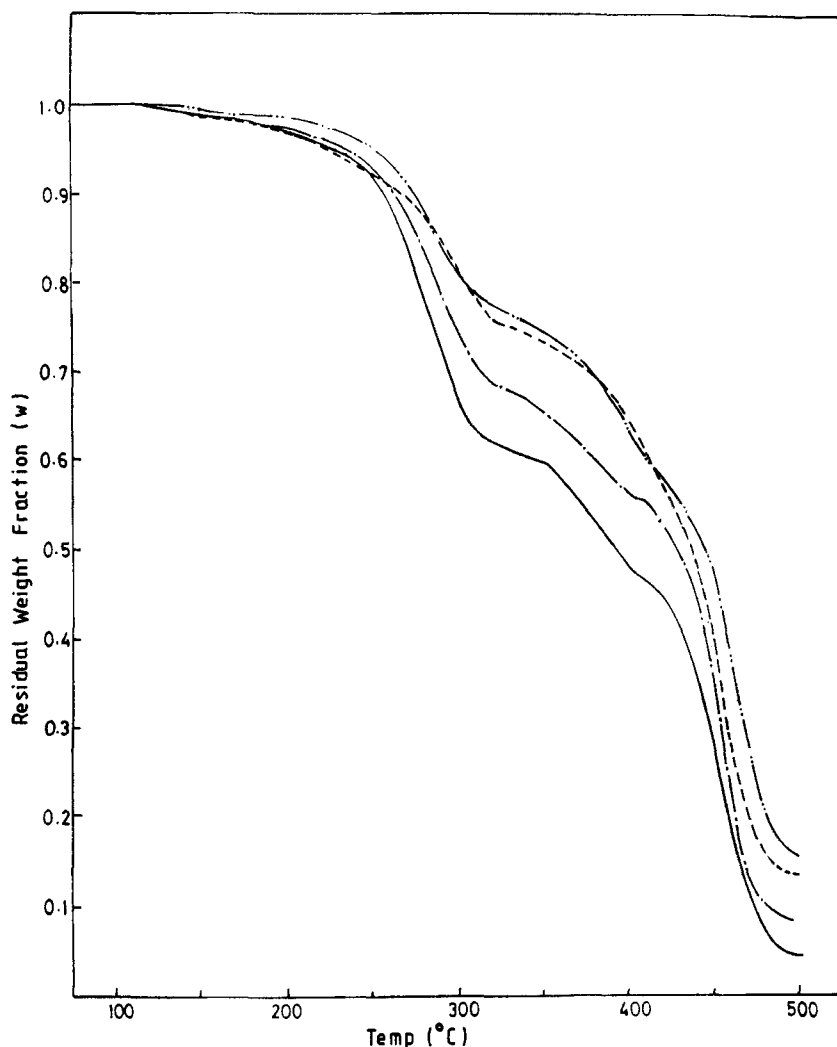given in Figs. 6 and 7. The various peak positions in the spectra of PMMA and PVP

FIG. 10.   TGA curves of iodinated copolymers of MMA/NVP. (— · · —) 20% of CP1, (— · —) 30% of CP1, (——) 40% of CP1, and (---) 20% of CP2.

are assigned to protons based upon the relative integration values and the peak positions reported in the literature [23]. The sharp peak at δ 3.6 is due to the —OCH$_3$ group of MMA; —CH$_2$ protons of MMA appear at δ 1.83 and α-methyl protons at δ 0.8–1.3. The peak at δ 2.07 represents the chain, and the center —CH$_2$ group of the pyrrolidone ring and the peaks between δ 2.2 and 3.5 arise from the —COCH$_2$, —CH$_2$N, and —CHN protons. These signals, characteristic of both MMA and NVP, clearly show their presence in the copolymers (CP1 and CP2). The main features of the NMR spectrum of 20% iodinated copolymer are: 1) —CHN and —CH$_2$N protons appear a little upfield, thus indicating that the nitrogen atom of the pyrrolidone group has acquired some positive charge; 2) besides the three
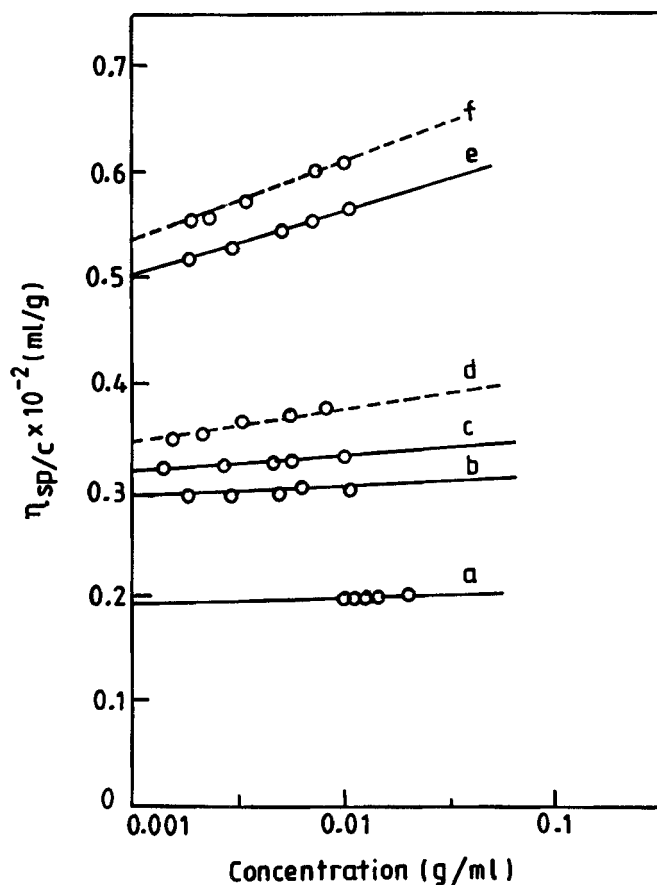
FIG. 11.   Reduced specific viscosity vs concentration of polymer solutions. (a) PVP,
(b) PMMA (c) CP1, (e) CP2, and (d, f) 20% iodinated products of CP1 and CP2, respec-
tively.

—CH$_3$ protons of MMA which are distinguished by a peak at δ 1.06, the other
proton peaks from the MMA and NVP units overlap and are not distinguishable;
and 3) the total number of protons based on the relative integration values is found
to be 26 instead of 17 protons for one unit each of MMA and NVP. Comparison of
the NMR peak positions of the prepared iodine complex with that of the commercial
PVP-I powder (Fig. 8) show that the positions of the rest of the peaks are similar in
the two spectra except the peak due to MMA methyl protons. The results point to a
bridge structure for the MMA/NVP copolymer–iodine complex in which two units
of NVP are linked to each other via a form of iodine.

Thermogravimetric Analysis and Differential Scanning Calorimetry

TG data of the samples are summarized in Table 5. Thermograms obtained by
plotting residual weight fraction vs temperature are presented in Figs. 9 and 10.

PMMA was found to decompose in two stages: the extents of first- and second-stage decompositions were 8 and 92%. According to available studies [24], PMMA prepared by free radical polymerization degrades in two stages; the extent of the first stage varying inversely with the molecular weight because the first stage is end-initiated at terminal unsaturated structures. The second higher temperature phase of reaction results from random scission initiation. Thus the TG behavior of PMMA shown in Fig. 9 is typical of a sample of the polymer of moderate molecular weight made by the free radical route. PMMA has a higher thermal stability than PVP, and because of higher NVP content in the copolymer sample CP1, the initial decomposition temperature for the first stage (IDT_1) of CPI is lower than that of CP2. But the second-stage decomposition starts at a higher temperature and IDT_2 values increase with increasing NVP content in the copolymer. For pure PMMA, the higher temperature phase of degradation which results from random scission of the polymer chain producing monomer is probably blocked by the presence of NVP in the backbone, thereby increasing IDT_2 and the final decomposition temperature. The values of IPDT, which are a measure of the thermal stability of a polymer, also increase with an increasing content of NVP in the copolymer. The IPDT values of CP1 containing different concentrations of iodine decrease with increasing iodine content of the sample, thus indicating that the overall thermal stability of the sample decreases after the incorporation of iodine into the copolymer.

DSC scans of the samples failed to show a single T_g, thereby confirming the fact that copolymer samples obtained by free radical polymerization of MMA and NVP are blends and not true homogeneous copolymers.

As expected, the viscosities of CP1 and CP2 were found to increase after incorporation of iodine into the samples (Fig. 11).

CONCLUSION

Because of the large disparity between the reactivity ratios, a copolymer of MMA and NVP with a homogeneous composition up to high conversion is difficult to obtain by free radical copolymerization. The polymers obtained are found to be blends, possibly consisting of PMMA and a nonhomogeneous copolymer of MMA–NVP with no PVP. Since the presence of the NVP unit is confirmed by various analyses, it can only be present in a copolymerized form with MMA. The polymer prepared takes up iodine with the formation of a stable complex which is insoluble but swellable in water and which liberates iodide ion in aqueous solution. These properties of the complex are essential for its use as a bactericide similar to the one earlier reported by us [25]. The ^{1}H-NMR spectrum of the complex does suggest a bridge structure for the complex involving two NVP units with their pyrrolidone carbonyl groups interacting specifically with iodine. We hope to add further information to the structure of the copolymer–iodine complex by studying the release mechanism of iodine from it and correlating a structure–antimicrobial property relationship.

ACKNOWLEDGMENT

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