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Effect of Structure of Polymeric Hindered Amines on the Oxidation of Polymers: Part 1—Syntheses of Polymeric Hindered Piperidyl Esters

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ABSTRACT

The polymerization of 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPM; I) and the copolymerization of TMPM separately with methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), 2-ethylhexyl acrylate (2-EHA), vinyl acetate (VAc), acrylamide (AAm) and styrene (St) were carried out in ethyl alcohol solution. The reaction of ester exchange does not occur. The new polymeric nitroxyl radicals were obtained by oxidizing the corresponding amines directly in alcoholic solution. Ester exchange of the copolymer of TMPM with VAc occurred during the oxidation in ethyl alcohol solution, and a water-soluble nitroxyl radical was obtained. The routes are simple and produce high yields. The melting points, solubilities, and thermogravimetric losses of the amines and nitroxyl radicals were determined, and the inhibitory effect of nitroxyl radical was also studied.

INTRODUCTION

Polymeric hindered amines are effective light stabilizers.[1] Conventionally, they have been synthesized in polar or nonpolar solvents, such as dioxane, dimethyl formamide, pyridine, acetic acid, benzene, chlorobenzene, toluene or petroleum ether. The products have been separated from polymerizate mixture solutions with various organic precipitants.[1–4]

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Polymeric hindered nitroxyl radicals are excellent stabilizers and inhibitors.[5,6] They may be prepared by the polymerization of monomer carrying the nitroxyl radical, the reaction of polymer with nitroxyl radical of lower molecular weight,[7] or the oxidation of the separated polymeric amine with hydrogen peroxide in methyl alcohol[2] or dioxane.[6] In this paper, ethyl alcohol was used as solvent and water as precipitant in the syntheses of polymeric amines. Polymeric nitroxyl radicals were synthesized simply from the corresponding hindered amines in alcoholic solution.

EXPERIMENTAL

Material

The preparation and purification of TMPM has been described.[8] Comonomers, azobisisobutyl nitrile (AIBN) and all the solvents were chemically pure reagents.

Polymerization

The reaction mixture, which contained 0·20 mol TMPM or 0·20 mol of TMPM with comonomer and 6·09 mmol AIBN in 70 ml ethyl alcohol, was placed in a three-necked flask under N_2. The flask was immersed in a thermostatted bath at 80 ± 0·1°C, polymerization was carried out under N_2 for a time required to obtain a high conversion and the mixture was precipitated in water. The precipitate was filtered, then dissolved. Purification of the polymer or copolymer was carried out by pouring its alcoholic solution into water, collecting the precipitate and drying *in vacuo* at 50°C or ambient temperature.

Oxidation of the polymeric hindered amines

To 100 ml of an ethyl alcohol solution containing 0·20 mol of the polymer of TMPM or the copolymer from 0·10 mol of TMPM and 0·10 mol of comonomer, a solution containing 36 ml of ethyl alcohol, 36 ml of 30% aqueous hydrogen peroxide and 10 mg sodium tungstate was added slowly at 30°C with stirring. The mixture was stirred for 2 h. The oxidation proceeds continuously at 30°C. The product was precipitated in water and the purification of the nitroxyl radical was carried out in the same way as for the amines. The TMPM—VAc product is soluble in water, and the separation of its nitroxyl radical was carried out by vaporizing solvent under reduced pressure.

Measurements

^1H—NMR spectra and ^{13}C—NMR spectra were obtained on a JEDL JUM-FX 100 spectrometer. Electron spin resonance (ESR) spectra were obtained by means of a Bruker ESR 300 spectrometer. Infrared spectra were recorded using a Perkin-Elmer 180 spectrometer, and the thermogravimetric analyses (TGA) were carried out with a Perkin-Elmer TGS-2 thermogravimetric analyzer under a dynamic nitrogen atmosphere at a heating rate of 10°C/min. Molecular weights of polymers were determined using a vapour-pressure osmometer (Knauer, Berlin) at 37°C in $CHCl_3$ with benzil as standard.

RESULTS AND DISCUSSION

Polymerization

Polymerization of TMPM was carried out under the given conditions for 4 h. The ^1H—NMR spectrum shown in Fig. 1 was determined in $CDCl_3$ at room temperature. TMS was used as the internal standard. The polymer of TMPM, polymerized in petroleum ether under the same conditions as that in ethyl alcohol, has a similar ^1H—NMR spectrum as that in Fig. 1. The results of elemental analyses are presented in Table 1. These results indicate that no ester exchange has occurred during the polymerization of TMPM in ethyl alcohol.

Copolymerization

Time-conversion rate curves for TMPM with St in ethyl alcohol are shown in Fig. 2. The conversion is increased with increasing TMPM/St ratio. This is as

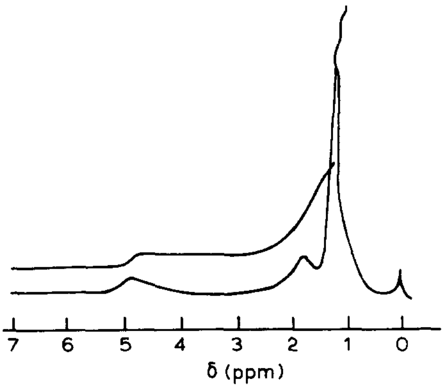

Fig. 1. The ^1H—NMR spectrum of the homopolymer of TMPM.

TABLE 1
Elemental Analyses of Poly-TMPM

Solvent[a]	*Result of elemental analyses (%)*			
	C	*H*	*N*	*O*
Ethyl alcohol	69·01	10·15	6·36	14·16
Petroleum ether	69·04	10·23	6·37	14·48

[a] Used in polymerization.

in the copolymerization in DMF.[4] The conversion rate for copolymerization of 4-methacryloxyl amino-2,2,6,6-tetramethyl piperidine with St is lower than that with MMA.[2] This may be due to complex formation between the radical and styrene, which leads to certain species which are relatively inactive in propagation.[9] At a reaction time of 2 h, the conversion is higher than 80%, so the ratio of TMPM/comonomer is 1, and the optimum copolymerization time is 2 h.

The copolymers were prepared under the conditions given above. Their ^{1}H—NMR spectra are shown in Figs 3 and 4, respectively. Figure 3 shows the methylene proton peaks at *c.* 4·08 ppm, but this peak does not appear in Fig. 4. These results again confirmed that there is no ester exchange during the copolymerization in ethyl alcohol.

The composition of the copolymers and the conversion of the TMPM and comonomers are given in Table 2. This shows that the ratios of TMPM/AAm and TMPM/VAc are higher in the copolymer than in the feed. This may be due to the reactivity ratios of methacrylate (M_1)—AAm(M_2) and methacrylate (M_1)—VAc(M_2) being $r_1 \gg 1$, $r_2 < 1$ respectively.[10]

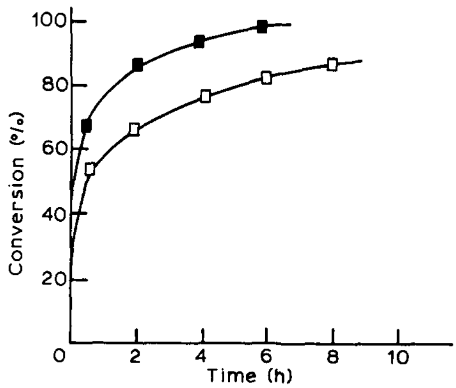

Fig. 2. Time–conversion curves for the copolymerization of TMPM with St: ■, TMPM/St = 1·0; □, TMPM/St = 1·0/1·5.

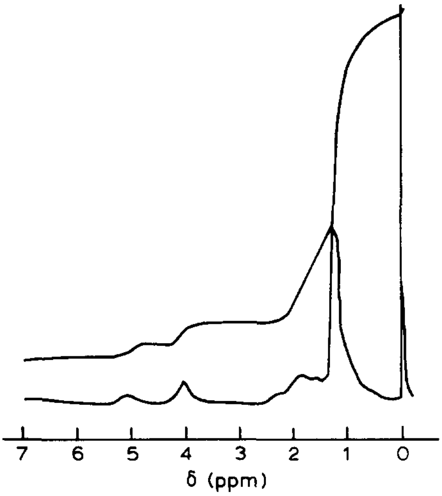

Fig. 3. The ^1H—NMR spectrum of poly (TMPM—CO—EA).

Polyacrylamide is a water-soluble polymer. Hindered amine is alkaline, and so poly (vinyl alcohol) may be obtained from poly (vinyl acetate) through ester exchange. Poly (vinyl alcohol) is a water-soluble polymer which disappeared during the synthesis of hindered amine.

Oxidation

Figure 5 shows the time–conversion curve for the oxidation of the copolymer of TMPM with St. It shows that the conversion is higher in ethyl alcohol than in dioxane; a time of 60 h was used for oxidation in alcoholic

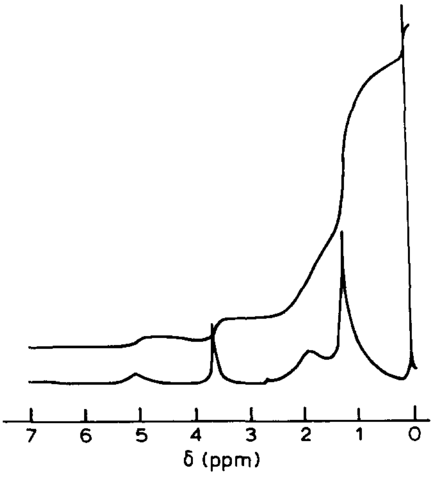

Fig. 4. The ^1H—NMR spectrum of poly (TMPM—CO—MA).

TABLE 2

Conversion of Monomers and Characteristics of Hindered Amines

Polymer	*N* (%)	*Composition*[a] *I/comonomer*	M_nX 10^{-3}	T_m^b (°C)	*Conversion*	
					I (%)	*I + Comonomer* (%)
I—I	6·29		5·2	146	99·8	
I—MA	4·65	1·13		120	92·8	89·8
I—EA	4·31	1·00	4·8	98	98·5	98·4
I—BA	4·18	1·17		68	91·6	86·9
I—2—EHA	3·42	1·10		45	85·4	85·4
I—MMA	4·26	0·97		149	87·2	87·9
I—EMA	3·67	0·89			91·6	95·4
I—BMA	3·67	0·91			92·6	95·9
I—St	4·27	1·01	3·9	127	84·8	84·5
I—VAc	5·28	2·02		132	98·8	84·2
I—AAm	7·84	2·31		168	82·6	71·4

[a] Ratio of chain elements in copolymer.

[b] Melting point.

solution in the following experiments. There is no ester exchange in the oxidation of copolymer except for TMPM with vinyl acetate in ethyl alcohol.

The IR spectra of the copolymer of TMPM with VAc were determined before and after oxidation. The results show that the bands at 1460 cm^{-1} (CH) and 1370 cm^{-1} (CH_3) decrease. The methylidyne and methyl are chained with acetoxy (CH_3COO) and carbonyl (C=O) respectively. The

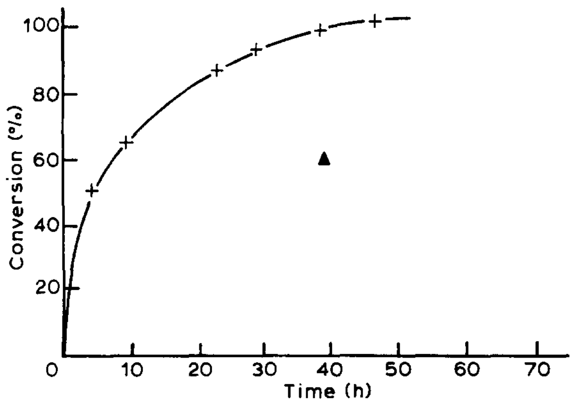

Fig. 5. Time–conversion curve for the oxidation of poly (TMPM—CO—St): TMPM/St = 1·0; +, ethanol; ▲, dioxane.

^{13}C—NMR spectrum of the copolymer of TMPM with VAc was obtained in CD_3Cl—CD_3COCD_3 (3:1) solution at 57°C. Resonances appear at 176·64, 176·40 and 176·47 ppm (ester carbonyl). After oxidation of the copolymer, its ^{13}C—NMR spectrum was determined, hexamethyl disiloxane (HMDS) being used as external standard in D_2O at the same temperature. ^{13}C—NMR resonances were exhibited only at 171·66 and 177·73 ppm (ester carbonyl).

The number of peaks for ester carbonyl in the ^{13}C—NMR spectrum decreased. This means that the ester carbonyl group in poly (TMPM—VAc) disappears during the oxidation.

According to the elemental analysis, the ratio of TMPM/VAc in the copolymer is 2·012. After oxidation the chain elements of TMPM and VAc were changed to nitroxyl radical (TMPM—NO$^{\bullet}$) and alcohol (V—OH), and the ratio of TMPM—NO$^{\bullet}$/VOH copolymer is 2·012. The elemental analysis results for this copolymer are:

Calculated: C, 64·10%; N, 5·34%; O, 21·34%.
Found: C, 63·82%; N, 5·43%; O, 21·09%.

These results show that ester exchange in the poly (TMPM—CO—VAc) during its oxidation in ethyl alcohol solution may occur.

The conversions for oxidation of polymeric hindered amines are given in Table 3. They are high. Like the polymeric hindered amines in Table 2, the melting temperatures of the nitroxyl radicals decrease with increasing number of carbon atoms in the ester groups of the comonomers, and are higher than those of the corresponding hindered amines. Polymeric

TABLE 3
Conversion of Amines and Characteristics of Polymeric Hindered Nitroxyl Radicals

Polymer	*N* (%)	*O* (%)	$M_n X$ 10^{-3}	T_m	*Conversion* (%)
II—II	6·00	19·90	—	166	99·6
II—MA	4·43	23·83	6·6	142	93·4
II—EA	4·20	23·43	7·0	132	98·4
II—BA	4·07	21·42	7·4	113	96·6
II—2—EHA	3·16	18·85	8·6	85	99·8
II—MMA	4·13	22·80	7·1	156	79·7
II—EMA	3·90	22·30	—	140	86·5
II—BMA	3·63	20·85	8·2	127	94·9
II—St	4·01	13·89	4·1	140	98·0
II—V—OH	5·43	21·24	—	137	80·9
II—AAm	7·48	20·30	—	—	99·8

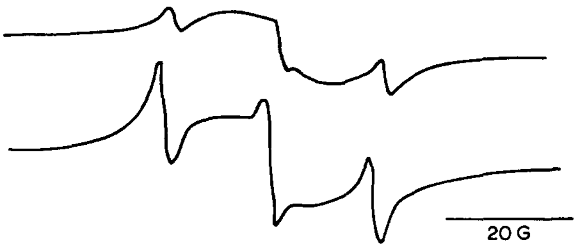

Fig. 6. ESR spectra of the nitroxyl radical of poly (TMPM—CO—2—EHA) (top) and poly (TMPM—CO—V—OH) (bottom).

hindered piperidyl esters melt at the temperature normally used for processing films, and they can be used as stabilizers.

The electron spin resonance (ESR) spectra of II—2—EHA and II—OH are recorded in Fig. 6. A clear triplet with components of equal intensities is observed. The hyperfine splitting constants (a_N) of some of the copolymers are summarized in Table 4. The values in the same solvent are approximately the same, however some differences were shown between the nonprotonic solvent, benzene, and certain protonic solvents such as methanol. The ESR spectrum of TMPM—BMA in dichlorobenzene solution is similar.[11]

Solubility

The polymeric hindered amines and nitroxyl radicals are soluble in ethyl alcohol, and all except $\left(\text{TMPM—NO}^{\cdot}\right)_{m}$ $\left(\text{V—OH}\right)_{n}$ are insoluble in water. They are soluble in chloroform and benzene with the exception of $\left(\text{TMPM}\right)_{m}$ $\left(\text{AAm}\right)_{n}$, $\left(\text{TMPM—NO}^{\cdot}\right)_{m}$ $\left(\text{AAm}\right)_{n}$ and $\left(\text{TMPM—NO}^{\cdot}\right)_{m}$ $\left(\text{V—OH}\right)_{n}$. These last three polymers are also insoluble in other

TABLE 4
Hyperfine Splitting Constants of Polymeric Hindered Nitroxyl Radicals at Room Temperature

Polymer	*Solvent*	a_N *(gauss)*
II—V—OH	Methanol	16·11
II—2—EHA	Methanol	16·16
II—2—EHA	Benzene	15·48
II—St	Methanol	16·16 16·3[a]
II—St	Benzene	15·42
II—MA	Benzene	15·37

[a] Reference 2.

solvents tested. Polymeric hindered nitroxyl radicals are more soluble in dioxane-1,4 than polymeric hindered amines, but in *n*-heptane, *n*-hexane, the order of solubility is reversed. Their solubilities in cyclohexane (solubility parameter = 8·2),[12] increase with increasing number of carbon atoms in the ester group of the comonomer, and this is also true for the amines or the nitroxyl radical as in Table 5. It is to be expected that the compatibility of I—St and I—2—EHA with polypropylene (solubility parameter = 8·2–9·2)[13] would be better than for the other esters.

The thermal stabilities of polymeric piperidyl esters are listed in Table 6. I—I, I—MMA and II—V—OH cannot be used as stabilizers for those fibers which have to be processed above 270°C.

Table 7 shows that the alkaline stabilities of polymeric hindered amine and nitroxyl radicals are good, and the stability of fibers containing these stabilizers against washing with detergents may be reasonable.

TABLE 5

Solubility of Polymeric Hindered Piperidyl Esters[a,b]

Polymer	*Solvent*[c]					
	n-Hexane (*7·3*)	*n-Heptane* (*7·4*)	*2-EHA* (*7·8*)	*Cyclohexane* (*8·2*)	*BA* (*8·8*)	*Dioxane-1,4* (*10·0*)
I—I	*	*	○	*	○	⊖
II—II	●	●	○	*	○	⊖
I—MA	*	*	○	*	○	●
II—MA	●	●	*	●	○	○
I—EA	⊖	⊖	○	○	○	⊖
II—EA	●	●	○	*	○	○
I—BA	○	○	○	○	○	○
II—BA	*	*	○	*	○	○
I—2—EHA	○	○	○	○	○	*
II—2—EHA	*	*	*	○	○	○
I—MMA	*	*	○	○	○	⊖
II—MMA	●	●	○	●	○	○
II—EMA	●	●	○	*	○	○
II—BMA	*	*	○	*	○	○
I—St	●	●	○	○	○	○
II—St	●	●	⊖	●	○	○
I—VAc	●	●	○	●	○	●
622[d]		●		●		○
944[d]		○		○		○

[a] 2·0 mg polymer in 2·0 ml solvent, at 25°C.

[b] ●, non-swelling; *, swells; ⊖, partially soluble; ○, soluble.

[c] Solubility parameters in parentheses (from Ref. 12).

[d] Tinuvin 622, Chimassorb 944; Ciba-Geigy products.

TABLE 6
Thermal Stability of Polymeric Hindered Piperidyl Esters

Polymer	*Weight loss (%)*				
	200°C	*225°C*	*250°C*	*275°C*	*300°C*
I—I	0·0	0·0	10·0	50·0	75·0
I—MA	0·8	0·8	3·0	8·0	21·0
I—EA	0·0	0·3	0·3	8·0	15·0
I—BA	0·0	1·0	3·0	10·5	20·0
I—2—EHA	0·0	0·0	0·8	6·0	18·5
I—MMA	0·0	0·0	8·0	78·0	—
I—St	0·0	1·5	4·0	13·0	28·0
I—VAc	1·0	1·0	2·0	11·0	34·0
I—AAm	4·0	5·0	6·5	10·0	19·0
II—II	0·0	0·0	3·0	17·0	43·0
II—MA	0·0	0·0	1·5	8·5	16·0
II—EA	0·0	0·0	2·0	9·0	16·0
II—BA	0·0	0·0	1·5	7·0	16·0
II—2—EHA	0·0	0·0	1·0	6·5	14·0
II—MMA	1·0	1·0	2·0	8·0	21·0
II—EMA	0·0	0·0	1·0	6·0	19·0
II—BMA	0·0	0·0	1·0	3·0	12·0
II—St	0·0	0·0	1·0	6·0	12·0
II—V—OH	17·0	18·0	20·0	25·0	37·0
II—AAm	4·0	5·0	6·0	7·0	24·0

TABLE 7
Alkaline Stability of Polymeric Hindered Nitroxyl Radicals

Polymer	*Before action*			*After action*		
	C (%)	*H (%)*	*N (%)*	*C (%)*	*H (%)*	*N (%)*
I—BA	66·33	9·82	4·12	67·59	9·90	3·82
II—EMA	64·39	9·41	3·90	64·95	9·22	3·85
II—BMA	65·92	9·60	3·63	65·95	9·55	3·73
II—St	72·82	8·88	4·11	72·93	8·82	4·13

TABLE 8
Inhibition of Polymeric Hindered Nitroxyl Radicals

Polymer	*Inhibitor*	*Inhibitor/ monomer*	*Yield (%)*	*B.P. (°C/mm Hg)*
Isobutyl acrylate	I—MA	0·10	95	62/50
Dimethyl-amino-ethyl acrylate	HQ[a]	0·50	65	70/15
Dimethyl-amino-ethyl acrylate	II—MMA	0·20	90	70/15
β-(ortho-acetoxy benzoxy)-ethyl acrylate	HQ	0·50	30	150/0·5
β-(ortho-acetoxy benzoxy)-ethyl acrylate	II—MMA	0·20	60	150/0·5
4,4′-diphenylmethane-diisocyanate	II—MMA	0·20	98	186/0·7
Pentaerythritol triacrylate	HQ, $CuCl_2$[b]	0·50	96	
Pentaerythritol triacrylate	II—V—OH[c]	0·20	99	
Acryloyloxy trimethoxy silicane[d]	II—2—EHA	0·20		

[a] Hydroquinone.
[b] Hardly washed.
[c] Easily washed out.
[d] Colorless liquid after a year.

The inhibitory action of polymeric hindered nitroxyl radicals are listed in Table 8. It may be noted that the nitroxyl radicals are effective radical traps even at high temperature. II—V—OH can be washed out with water after use.

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