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Synthesis, characterization and stabilization of poly(methyl glyoxylate)

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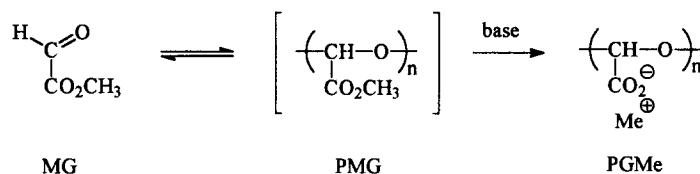
Poly(methyl glyoxylate) (PMG) is a biodegradable polyacetal. Its low ceiling temperature requires end-capping extremities. Until now, esterification and etherification were the main ending reactions used, but the results were inconclusive. Using functional isocyanates having alkoxysilane, methacrylic, styrenic or isocyanate functions, the end-capping is complete and no depolymerization occurs. Thermal stability of these new end-capped PMGs has been performed. Whereas, degradation begins at 67°C for non-terminated PMG, stabilized PMG can be stable up to 177°C. Physicochemical characteristics of the chains are given according to the chemical nature of the extremities. In particular, we can notice an important effect on glass transition temperature at low molecular weight with a discrepancy of about 20°C between the silane and methacrylic extremities. © 1997 Elsevier Science Ltd.

(Keywords: end-capped poly(methyl glyoxylate); thermal stability; glass transition temperature)

INTRODUCTION

Methyl glyoxylate (MG) was first polymerized by Monsanto Co.[1-3] to lead to alkali metal polyglyoxylate (PGMe) via poly(methyl glyoxylate) (PMG) according to the following mechanism:

molecular weight. Monsanto[5-8] used etherification or esterification as end-capping reactions. Initially, we repeated these reactions and spontaneous depolymerization still occurred in diluted media or at room temperature, and thermal stability was not improved. Consequently, we perfected the end-capping by using heterofunctional

MG   PMG   PGMe

The industrial use of PGMe is as a biodegradable detergent builder or complexing agent. Nevertheless, industrial development has been limited due to its low molecular weight, low thermal stability and spontaneous depolymerization from hydroxyl extremities at room temperature. Moreover, the polyacetal backbone of the polymer is very sensitive to acidic media. Our interest in this type of polymer came from its biodegradability[4]. Glyoxylic acid, the ultimate derivative stemming from degradation, is a Krebs metabolite, in particular in the vegetable cycle. Whatever the patent, the polyester PMG itself was never isolated and its stability and chemical properties never investigated. In this study, our purpose is to isolate the hydrophobic PMG and to enhance its thermal stability for agrochemical, pharmaceutical or medical uses as a hydrophobic matrix for the controlled release of drugs or for a biodegradable coating in the encapsulation process. Thus, we have first focused our attention on stable end-capping of PMG chains in order to obtain thermally stabilized material with sufficient

reagents which always contain an isocyanate function. In each case, isocyanates react quantitatively with hydroxyl extremities and lead to a polymer bearing a new reactive function which can be subsequently used to modulate the biodegradable matrix properties by chain extension, crosslinking or copolymerization.

EXPERIMENTAL

Materials

MG was kindly supplied by Société Française Hoechst. Ethyl vinyl ether (EVE), 3,4-dihydro-2*H*-pyrane (DHP), acetic anhydride (AA) and hexamethylene diisocyanate (HMDI) were purchased from Aldrich. 2-Methyl-2-propenoyl isocyanate (MAI) (SNPE), isocyanatopropyltriethoxysilane (SiNCO) (Interchim) and {1-methyl-1-[3-(2-propenyl)phenyl]}ethyl isocyanate (TMI) (Cyanamid) were used as supplied.
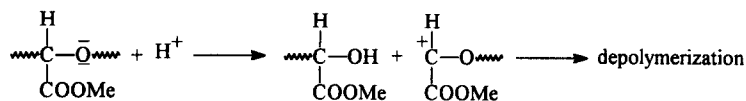
Thermal analysis

Thermogravimetric analysis (t.g.a.) studies were carried out with a thermogravimetric analyser TGA 7
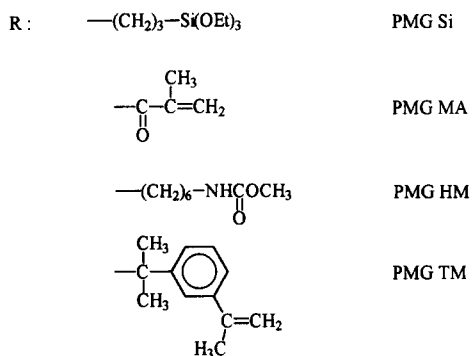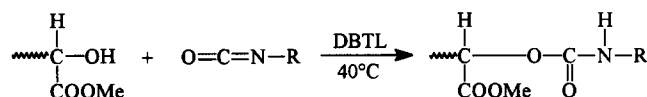
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$$CH_2=CH—OC_2H_5 \xrightarrow{HCl} CH_3—\overset{+}{C}H—OC_2H_5$$
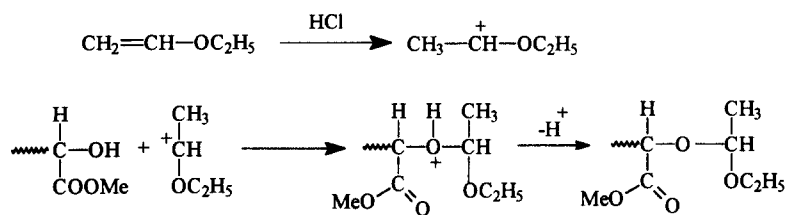
Scheme 1

Scheme 2

Scheme 3

(Perkin Elmer). The heating rate was $20°C\,min^{-1}$ from room temperature to 350°C under N_2 and the samples weighed about 10 mg. Isothermal measurements at different temperatures *versus* time were performed on the same apparatus.

Differential scanning calorimetry (d.s.c.) studies were carried out with a DSC 7 (Perkin Elmer). The heating rate was $10°C\,min^{-1}$ and the samples weighed about 8 mg. Calibration was achieved with indium as reference material. The reported T_g were taken at the middle point of the curve.

Nuclear magnetic resonance (n.m.r.) studies

The n.m.r. spectra were recorded on Bruker AC (200 MHz) and AM (360 MHz) instruments at 25°C using $CDCl_3$ as solvent and locking agent. An inverse gated sequence, with a relaxation delay of 10 s, was used to allow quantification of extremities.

Size exclusion chromatography

Molecular weights were obtained by size exclusion chromatography (s.e.c.) in dichloromethane using a Waters pump model 6000, injector (Rheodyne) and refractive index detector (RID-6A Shimadzu), equipped with two PL gel $5\,\mu m$ mixed-C linear columns. The system was calibrated using polystyrene standards with low polydispersity.

End-capping reactions

Endcapping by ethers and ester was taken from Monsanto patents[5-8]. For condensation with isocyanates, a typical procedure is as follows: to a 5 M solution of PMG in dichloromethane, in a 50-ml round bottom flask, under argon, isocyanate in double excess is added through a septum (for reaction with hexamethylene diisocyanate, a 10% excess is used). Dibutyltin dilaurate (3 drops) is used as catalyst. The reaction mixture is stirred for 48 h at room temperature and 12 h at 40°C. At the end of the reaction, methanol is added to destroy the isocyanate in excess. The solution is then poured into methanol and a white precipitate of PMG is recovered from the solution. The polymer is washed twice in dichloromethane and methanol and finally dried *in vacuo* at room temperature during 24 h.

RESULTS AND DISCUSSION

Monsanto patents[9-11] described homopolymerization of MG by different initiators. In this study, PMG was prepared by anionic polymerization of MG using freshly distilled triethylamine (Fluka) as initiator and dried dichloromethane (SDS) as solvent. The procedure for the synthesis was described elsewhere[12-14]. Triethylamine was chosen for its good miscibility with the monomer and its ease of use. Moreover, CH_2Cl_2 leads to higher molecular weight ($DP_n \approx 100$) than tetrahydrofuran ($DP_n \approx 75$) or ethyl acetate ($DP_n \approx 58$) with an optimum polymerization temperature of $-20°C^5$.
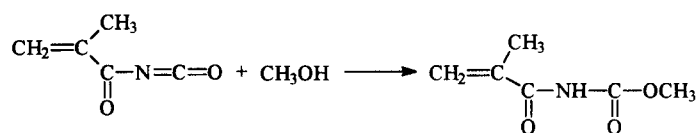
In order to end-cap hydroxyl extremities, the literature gives tables of various termination reagents[5-8]. Most of these products were tested by Muller[12] and by ourselves. In this work, we report the reactions of EVE, DHP and AA, which were used without success since depolymerization still occurred. Only isocyanate end-cappings led to the expected results.

End-capping by ester and ethers

The reaction was carried out directly at the end of polymerization in CH_2Cl_2 with 1 N HCl as catalyst. EVE, DHP and AA have been used according to *Scheme 1* (e.g. reaction with EVE).

Acidic attack of the acetal chain by protons of the catalyst was also observed. This reaction leads to chain depolymerization in the solution and release of MG (*Scheme 2*).

Proton n.m.r. analysis confirms the presence of aldehydic monomer at 9.4 ppm in the resulting solution

$$CH_2=C \overset{CH_3}{\underset{\underset{O}{\overset{\|}{C}}-N=C=O}{}} + CH_3OH \longrightarrow CH_2=C \overset{CH_3}{\underset{\underset{O}{\overset{\|}{C}}-NH-\underset{O}{\overset{\|}{C}}-OCH_3}{}}$$

Scheme 4

Table 1 Molecular weight measurements

Technique	PMG Si		PMG MA	
	1	2	1	2
S.e.c.[a]	5500	34000	3000	32500
S.e.c.[b]	5600	34000	7000	32500
^{13}C n.m.r.	4600	15100	2900	17000
Si dosage	4000	10000	—	—

[a] Before endcapping
[b] After endcapping

Table 2 Thermal stability of different end-capped PMGs. T_s: temperature of the start of degradation; T_{max}: temperature of maximum rate of degradation

	T_s (°C)	T_{max} (°C)
PMG.OH	67	164
PMG.DHP	110	148
PMG.EVE	112	155
PMG.AAc	113	163
PMG.HM	177	255
PMG.MA	130	202
PMG.Si	135	250
PMG.TMI	132	232

either from depolymerization of a non-terminated extremity or acidic attack of the polymer backbone. Total end-capping of the chains was never reached by using EVE, DHP or AA whatever the reaction time (from 1 to 24 h) or temperature (ambient to 40°C). Moreover, the second reaction is favoured and yields a decrease when the time of reaction or temperature increases.

End-capping by isocyanates

Isocyanates react with hydroxyl extremities of PMG and lead to stable urethane bonds as depicted in *Scheme 3*.

The amount of isocyanate used depends on the average molecular weight of the chains $(\overline{M}_n)$. The $\overline{M}_n$ values are determined by s.e.c. in dichloromethane immediately after polymerization. A double excess is used for reactions with SiNCO, MAI, TMI and only a 10% excess for HMDI to avoid side reactions like crosslinking on N–H groups. However, in the last case, an increase in chain length is observed when HMDI is not used in excess.

With HMDI, the second isocyanate extremity was converted into urethane during precipitation in methanol. The ^{1}H n.m.r. analysis does not show any signal of aldehydic hydrogen at 9.4 ppm, attesting that the reaction is complete. Average yields after precipitation and filtration of modified polymer are about 80%.

Characterization of the end-capped chains

^{13}C and ^{1}H n.m.r. The ^{1}H n.m.r. spectrum of PMG before end-capping (PMG.OH) does not show any signal for hydroxyl extremities (CH acetal: 5.6 ppm; OCH$_3$ ester: 3.8 ppm). However, an aldehyde signal is present

at 9.4 ppm due to the polymerization/depolymerization equilibrium. The ^{13}C n.m.r. spectrum of the polymer backbone exhibits three peaks (C=O: 165 ppm; C acetal: 91 ppm; OCH$_3$: 51 ppm). For isocyanate end-capped polymers, additional chemical shifts are observed typical of the extremities (m = multiplet):

^{1}H n.m.r.: PMG.HM $((CH_2)_6$: (m) 1.2 ppm; NH: 6.2 ppm), PMG.MA (CH$_3$: 2 ppm; NH: 6.2 ppm), PMG.Si (CH$_3$CH$_2$O: (m) 0.8–1.7 ppm; NH: 6.2 ppm), PMG.TMI (CH$_3$: (m) 1.7 ppm; H aromatic: (m) 7.3 ppm).

^{13}C n.m.r.: PMG.MA (methacrylic CH$_3$: 16 ppm), PMG.Si (CH$_3$CH$_2$O: 18 ppm; CH$_3$CH$_2$O: 57 ppm).

We only report chemical shifts of the best resolved peaks. For example, in the case of PMG MA the signal-to-noise ratio was too low to assign definitively the peaks for double bonds.

Molecular weight measurements

The s.e.c. measurements have been performed for all samples, before and after end-capping. $\overline{M}_n$ values obtained by s.e.c. rise from 3000 to 40000. The polydispersity of the samples varies between 1.3 and 1.7. No change in molecular weights was noticed after functionalization (e.g. *Table 1*: PMG.Si samples 1 and 2; PMG.MA in sample 2). This result is of the highest importance for PMG.MA because it implies that the experimental conditions do not lead to polymerization of methacrylic double bonds. Thus, when PMG of low molecular weight $(\overline{M}_n = 4000)$ is modified by MAI, there is no reason to observe methacrylic polymerization. Nevertheless, s.e.c. measurements exhibit an apparent increase in molecular weight after end-capping (*Table 1*: PMG.MA sample 1). Moreover, the ^{1}H n.m.r. spectra of PMG.MA of low molecular weight in CDCl$_3$ reveals the presence of nearly 6 ppm of a broad signal corresponding to the methacrylic CH$_2$ extremity. Our interpretation of increasing molar mass comes from an aggregation of the extremities resulting from poor solvation in dichloromethane. The broadness of this signal agrees with this poor solvation of the extremity in CDCl$_3$ and aggregations of the double bonds as above mentioned.

On the basis of this assumption, an additional test was performed and consisted of preparing a solution of low molecular weight PMG.MA in CH$_2$Cl$_2$ and adding MAIMe which is the shortest molecule representative of the MAI extremity. This model was synthesized by condensation of methanol in excess and MAI (*Scheme 4*).

This compound crystallizes from the methanol solution and is totally insoluble in MAI, PMG.OH or in any usual solvent, in particular CH$_2$Cl$_2$. Thus, s.e.c. and ^{1}H n.m.r. studies of this compound, could, therefore, not be achieved. Nevertheless, MAIMe is soluble (about 10%, w/w) in the aggregates of low molecular weight PMG.MA in CH$_2$Cl$_2$.

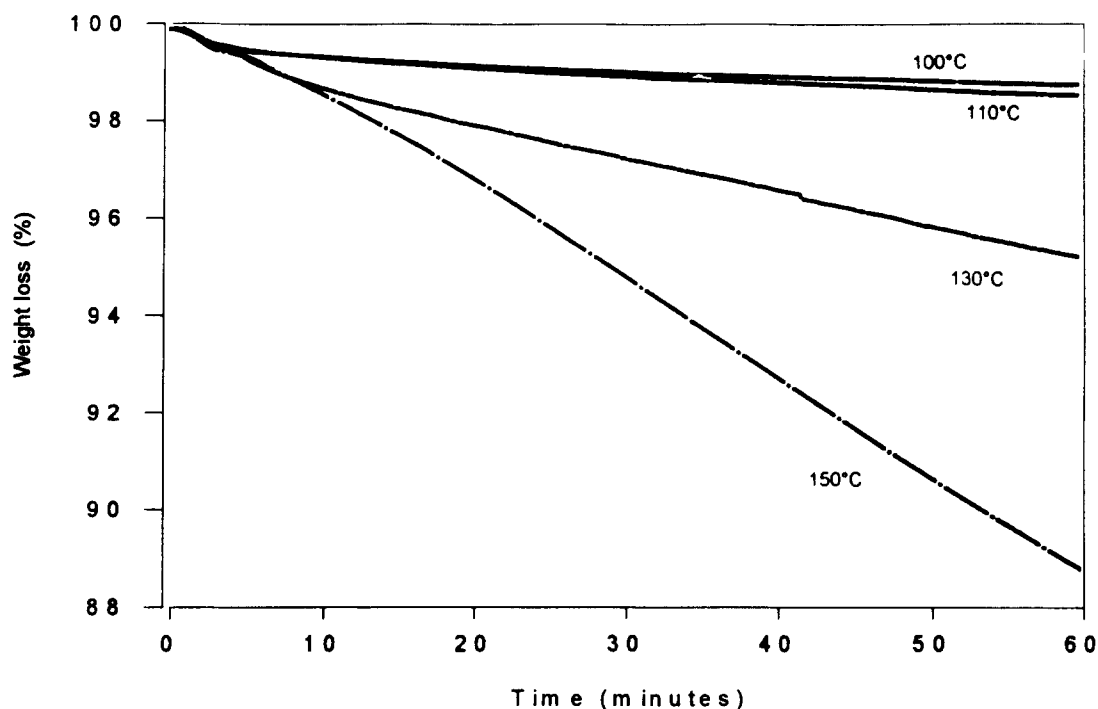All these results confirm the presence of associated phenomena due both to the poor solvation and to the

Figure 1 Thermal degradation of PMG.HM ($\overline{M_n}$ = 12 000) at 100, 110, 130 and 150°C
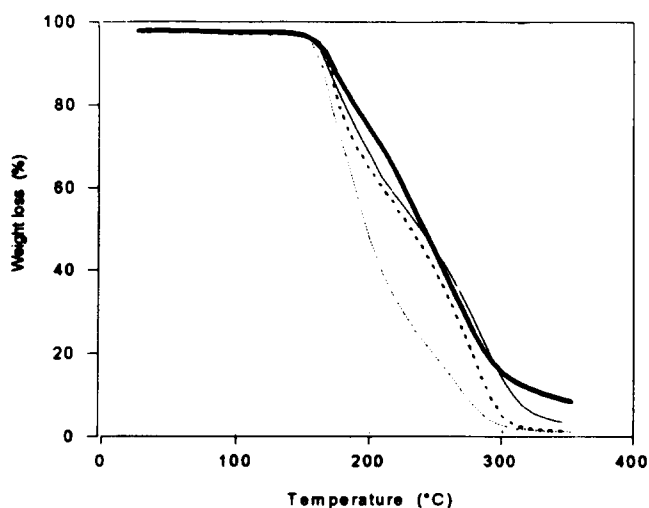

Figure 2 Thermal degradation *versus* temperature of a series of PMG.MAs (———: $\overline{M_n}$ = 4000; ———: $\overline{M_n}$ = 8600; ·····: $\overline{M_n}$ = 17 000; — — —: $\overline{M_n}$ = 40 000)

high concentration of the extremities in the medium. Inversely, when $\overline{X_n}$ increases, MAI extremities are well dispersed in the medium and s.e.c. results are not affected.

Comparison of measurement techniques

Molecular weights after functionalization have been measured by [13]C n.m.r., s.e.c. in dichloromethane and dosage of Si for SiNCO end-capped chains. Two samples of PMG.MA and PMG.Si were analysed by these techniques. The $\overline{M_n}$ are determined from [13]C n.m.r. inverse gated spectra, which give a quantitative analysis of the signal. The results are presented in *Table 1*.

For low molecular weight polymers (samples 1), values obtained by s.e.c. before condensation and after condensation (except for PMG.MA as explained above), [13]C n.m.r. and dosage of Si are similar. Calibration of

the columns with polystyrene standards can then be considered as a valid system.

However, for higher molecular weights (samples 2), $\overline{M_n}$ obtained by s.e.c. are two or three times higher than those obtained by [13]C n.m.r. or dosage of Si. On the one hand, we attribute this difference to the lack of sensitivity of these latter methods when the chain length increases. On the other hand, these results can reveal the deviation between the calibration curve established from polystyrene standards and the true one for modified PMG.

Thermal properties of end-capped PMG

Thermal stability was studied by t.g.a. The temperature of the start of degradation, T_s, and of the maximum rate of degradation, T_{max}, for various end-capped chains are given in *Table 2*. Average molecular weights are about 10 000 for all polymers.

Weaker thermal stability is observed for chains with hydroxyl extremities (PMG.OH; $T_s = 67°C$). Although total end-capping by ether or ester is never reached (PMG.DHP, PMG.EVE, PMG.AA), nevertheless, thermal stability is improved and T_s rises to about 110°C, but this value is still lower than thermal stability values observed for isocyanate end-capped chains. In these cases, degradation does not occur before 130°C and T_{max} widely exceeds 200°C except for PMG.MA. From these results it can be seen that using isocyanate extremities avoids depolymerization and clearly improves the thermal stability of PMG.

We have particularly focused our interest on PMG.HM because it shows the best thermal stability among all these polymers. The degradation behaviour of PMG.HM ($\overline{M_n}$ = 12 000) was also investigated *versus* time (*Figure 1*), at various temperatures (T = 100, 110, 130 and 150°C).

The first weight loss ($\approx 0.5\%$) is attributed to residual water in the polymer powder. At 100 and 110°C, weight loss is limited to about 0.5% in 1 h, but, for higher
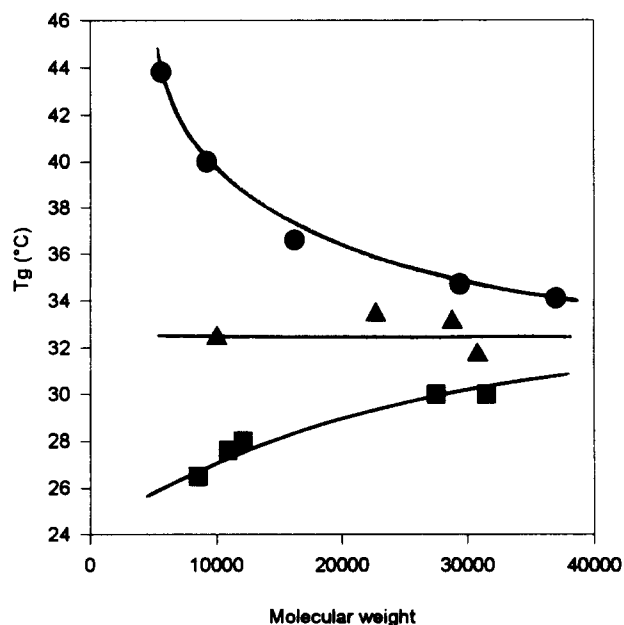
Figure 3 Glass transition temperature *versus* $\overline{M}_n$: (■) PMG.Si; (▲) PMG.HM; (●) PMG.MA
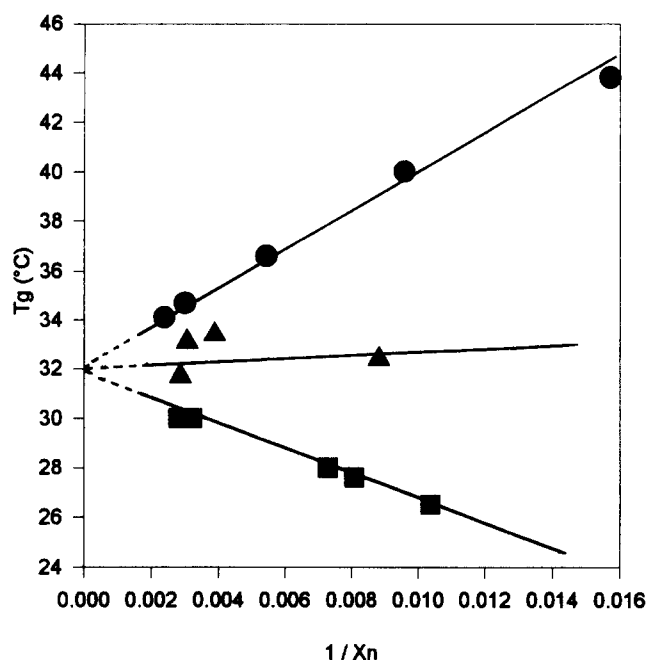

Figure 4 Glass transition temperature *versus* $1/\overline{X}_n$: (■) PMG.Si; (▲) PMG.HM; (●) PMG.MA

temperatures, degradation rates are much more important (4% at 130°C and 10.5% at 150°C). These values are very useful in determining the upper limit of use for this polymer.

We also investigate the influence of molecular weight on thermal stability for PMG.MA, PMG.HM and PMG.Si. *Figure 2* shows weight loss *versus* temperature for a series of PMG.MA ($4000 < \overline{M}_n < 40\,000$).

The general trends of these curves are the same, but uncontrolled variations are observed (e.g. $\overline{M}_n = 17\,000$). Whatever the nature of the extremity, in this range of $\overline{M}_n$ no relevant change in T_s was noticed.

Glass transition temperature of PMG isocyanate end-capped

The relation between properties and degree of polymerization of low molecular weight polymers or copolymers has received considerable attention in the last few years. The $T_g = f(\overline{X}_n)$ relation of linear polymer systems has been widely studied by estimating the asymptotic T_g value at high molecular weights and taking into account the T_g deviations from that value at lower molecular weights. It is a common view that the T_g value must decrease on decreasing the molecular weight (negative deviation) because of the progressive loss of the cohesive state of the system due to the greater mobility of the end units compared to those of the molecular backbone, when the end groups have chemical similarity to the repeating units.

However, many polymeric systems have end units or groups which are chemically different to those of the molecular body. A definite end effect of a chemical dissimilarity of end units was studied by Ueberreiter and Rohde-Liebenau[15] on polystyrenes having trichlorotriphenylmethyl groups. They found some slightly positive T_g deviations from the asymptotic value with decreasing chain length, instead of marked negative deviations, as expected for classical polystyrenes. Recently, Danusso *et al.*[16] working on perfluorinated oligomers with different end groups ($-CH_2OCH_3$, $-CH_2OSi(CH_3)_3$, $-CH_2OCOCF_3$, $-CH_2OH$ and $-CH_2OK$) found marked positive deviations for the diolic and $-CH_2OK$ series.

The T_g measurements were performed by d.s.c. on three series of PMG (MA, HM and Si) of different molecular weights. After a cooling run from 60 to $-20°C$, T_g values were determined from the second run (-20 to 60°C at $10°C\,min^{-1}$). All the $\overline{M}_n$ data were determined by s.e.c. in dichloromethane. The data relating to these series are graphically represented in *Figure 3* as a function of $\overline{M}_n$.

From our results it immediately appears that the $T_g = f(\overline{M}_n)$ relation for a given polymeric system can be heavily modified by changing the chemical nature of the end groups. Moreover, both positive and negative T_g deviations can take place.

On the one hand, the PMG.Si series shows a classical behaviour (negative deviation) as described in previous literature on other systems. On the other hand, the PMG.MA series shows a positive deviation and for the PMG.HM series, the T_g deviation is not significant. *Figure 4* shows the T_g data relating to the three series when plotted according to the well known Fox and Flory relation:

$$T_g = T_{g\infty} - \frac{K}{\overline{X}_n}$$

These data are well represented by straight lines whose slopes depend on the nature of the chemical extremities. These three series must show the same limit when $\overline{M}_n$ rises to infinity ($T_g = 32°C$). We attribute the increase in T_g for the PMG.MA series to the stiffness of the conjugated double bonds present in methacrylic extremities. Moreover, we previously described (s.e.c. study) the aggregation of the MAI extremities. The contribution of aggregation phenomena could also explain the observed increase of T_g as $\overline{X}_n$ decreases.

Concerning the invariability of the glass transition temperature of PMG.HM chains, the flexibility of

methylene groups probably compensates for the stiffness of the urethane groups.

CONCLUSION

By using isocyanates as end-capping reagents, PMG is thermally stabilized and no depolymerization occurs. The choice of isocyanates having alkoxysilane, methacrylic, styrenic or isocyanate functions allows us to consider the possible copolymerization and/or the cross-linking of these modified PMGs. Degradation studies on PMG in the solid state under different experimental conditions will be reported soon.

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