Synthesis and characterization of monoalkyl maleates and their use in emulsion polymerization of vinyl acetate

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SUMMARY: Different monoalkyl maleates (MAM) have been synthesized and used as functional (co)monomers in the emulsion polymerization of vinyl acetate (VAM). Vinyl acetate was added either in batch or semicontinuously in order to improve the incorporation yield of the comonomers. The monoalkyl maleates and the different latexes obtained were fully characterized using nuclear magnetic resonance spectroscopy (^{1}H NMR and ^{13}C NMR), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). We demonstrated that the monoalkyl maleates were entirely reacted and incorporated in the copolymers. When using a semi-continuous addition process for vinyl acetate, it was found that the monoalkylmaleates were mostly contained into copolymers which are extractable from the latex particles by centrifugation. We showed that these extractable copolymers contain around 28 weight percent of monoalkyl maleate which concentration is larger than the concentration of monoalkyl maleate in the feed. The incorporated monoalkyl maleates contribute to a decrease of the glass transition temperature of the copolymers.

Introduction

Researches in order to improve the properties of poly(vinyl acetate) and its copolymers as for instance adhesion, plastification and stability, are still of great interest. So far, different functional monomers, like acrylic acid and methacrylic acid, have been used which present the disadvantage to homopolymerize in water and, consequently, to be poorly incorporated in the latex particles [1, 2]. Other efforts have been made for internal plastification with the use of vinyl esters as for example VeoVa that proved to improve significantly the overall latex properties such as hardness, flexibility, alkali and water resistance [3]. The internal plastification of poly(vinyl acetate) copolymers has also been achieved using diesters of the maleic anhydride such as dibutyl maleate [4]. When compared to the use of external plasticizers as for instance dioctylphtalate, the main advantage of the alkyl maleates is that they can be more strongly associated to the latex particles and are consequently more stables

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time. It is then expected that the final properties of the copolymers will be enhanced and will not be altered during time due for instance to the migration of the plasticizer. In recent works, new functional and reactive monoalkyl maleates have been synthesized and characterized [5]. Monoalkyl maleates containing polymerizable groups provide enhanced stability under shear stress or freeze-thaw conditions. In addition, they have proved to be useful in the preparation of protective coatings which were developed by solution polymerization techniques. These coatings provide effective protection against damage caused by weathering, contamination from the atmosphere and chemical attack. The principal structural characteristics of monoalkyl maleates are the presence of one carboxylic group, one ester group and the double bond. The maleic derivatives are easily copolymerized but cannot homopolymerize. In the present work the hemiesters synthesized were based upon butanol, dodecanol and hexadecanol. They were fully characterized and used in emulsion copolymerization with vinyl acetate. The ensuing materials were characterized using DSC and NMR techniques.

Experimental

All the reagents used in the present study were of analytical grade (from Aldrich). Maleic anhydride, butyl alcohol, dodecyl alcohol and hexadecyl alcohol, vinyl acetate (**VAM**), potassium meta-bisulfite and potassium persulfate were used as received. The nonylphenol ethoxylated non ionic surfactant (**A-103**) was from CYTEC.

Synthesis of the monoalkyl maleates

A typical reaction scheme for the synthesis of the monoalkyl maleates is given in Figure 1.

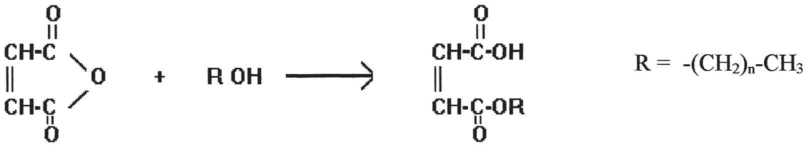

Fig. 1. Reaction scheme for the synthesis of the monoalkyl maleates. n = 3, 11 and 15 corresponds to the chain length of the alkyl group.

a) Synthesis of mono butyl maleate (MBM)

Maleic anhydride (220.5 g) was fused at 65°C and the butyl alcohol (104 g) was added continuously during 3 hours. The mixture was stirred (100 rpm) for 2 more hours at 65°C. Finally, a viscous yellow liquid was obtained.

b) Synthesis of mono dodecyl maleate (MDM) and mono hexadecyl maleate (MHM) [5]

Maleic anhydride (49g) and the alcohol (1-dodecanol (96g) or hexadecyl alcohol (170g)) were stirred in the melt at 80°C for one hour. 300 ml of heptane were added to the reaction mixture and stirred for some minutes until an homogeneous solution was formed. The solution was kept at room temperature for three hours and then cooled down at 15°C for two hours. The precipitate formed was collected and recrystallized from heptane. White bright crystals of MDM or MHM were obtained, respectively.

Emulsion copolymerization of vinyl acetate and monoalkyl maleates

Polymerization was carried out at 70°C in a glass reactor under stirring (100 rpm) and under a stream of nitrogen. First, the monoalkyl maleate was dissolved in water at pH 5. The surfactant and the redox initiator (potassium persulfate / potassium metabisulfite) were added all at once. This procedure resulted in a homogenous mixture. Subsequently, vinyl acetate was added following a semi-continuous (for 2 hours) or batch procedure. Purification of the polymers prior to characterization was done using the following conditions: centrifugation at 15 000 rpm for 2 hours, separation of the polymer from the liquid part and drying at 70°C for 48 hours. The solid content of the latex was around 30 wt%.

Characterizations

^{1}H and ^{13}C NMR spectra were recorded on a VARIAN model Unity Inova spectrometer at 300 MHz. $CDCl_3$ was used as solvent and trimethylsilane as internal standard. The melting point, Tm (°C), and the free enthalpy of melting, ΔHm, of the hemiesters were determined by DSC (DSC 101, Setaram) following the ASTM 1269-89 method. The typical sample weight was 10 mg. The temperature range used was from 0°C to 80°C with a heating rate of 2°C/min. The glass transition temperature of the copolymers, Tg (°C), was determined also by DSC (DSC 101 Setaram). The typical sample weight was 15 mg. All samples were analyzed from -40°C to 100°C with a heating rate of 10°C/min. Monomer conversion was determined

Molecular weights and molecular weight distributions were determined by GPC (Waters 490 E programmable multi-wavelength detector) following the ASTM D3536-91 and ASTM D3016-78 methods (Ultrastyragel column, THF eluent) and using polystyrene standards.

Results and discussion

Synthesis and characterization of the monoalkyl maleates

Table 1 shows the results concerning the synthesis and characterization of the monoalkyl maleates. The degree of purity of the monoesters was checked by NMR by comparing the experimental peak integral at 4.2 ppm to the theoretical value (see Fig. 2 and Table 2). The results in Table 1 and Table 2 indicate that nearly pure monododecyl and monohexadecyl maleates were obtained in good yields. Purification of the monobutyl maleate appeared to be more difficult to perform in good conditions due to the liquid character of the monoester and considering the solubilities of the reactants and products that are very similar. The products of the reaction were indeed a mixture of butanol, maleic anhydride, dibutyl maleate and monobutyl maleate. The ^1H NMR and ^{13}C NMR spectra of the monohexadecyl maleate are given in Fig. 2 and Fig. 3, respectively.

Table 1. Physical properties and characteristics of the monoalkyl maleates.

Samples	Color	Aspect	Tm (°C)	ΔHm	Yield (%)	Purity (%)
MBM	Yellow	Liquid	-	-	70	68
MDM	White	Solid	52	96	98	97
MHM	White	Solid	71	97	98	98

Table 2. ^1H NMR analysis of the monoalkylmaleates

Sample	Integration	CH_3 (a)	$(CH_2)_n$ (b, c)	O-CH_2 (d)	CH = CH (e)	OH
MBM	Theoretical	3.0	6.0	2.0	2.0	1.0
	Experimental	3.1	4.1	2.0	1.9	0.8
MDM	Theoretical	3.0	20.0	2.0	2.0	1.0
	Experimental	3.0	19.7	2.0	2.0	0.9
MHM	Theoretical	3.0	28.0	2.0	2.0	1.0
	Experimental	2.7	27.0	2.0	1.9	1.0

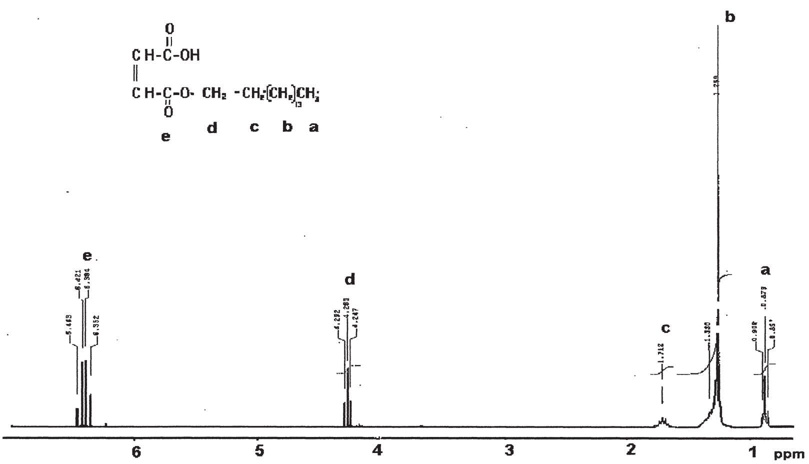

Fig. 2. ^{1}H NMR spectrum of the monohexadecyl maleates (MHM). δ ppm: 0.857 (3H, CH_3); 1.25 (26 H, $(CH_2)_{13}$); 1.712 (2H, CH_2); 4.247 (2H, CH_2O); 6.35 (1H,=CH), 6.42 (1H, = CH)

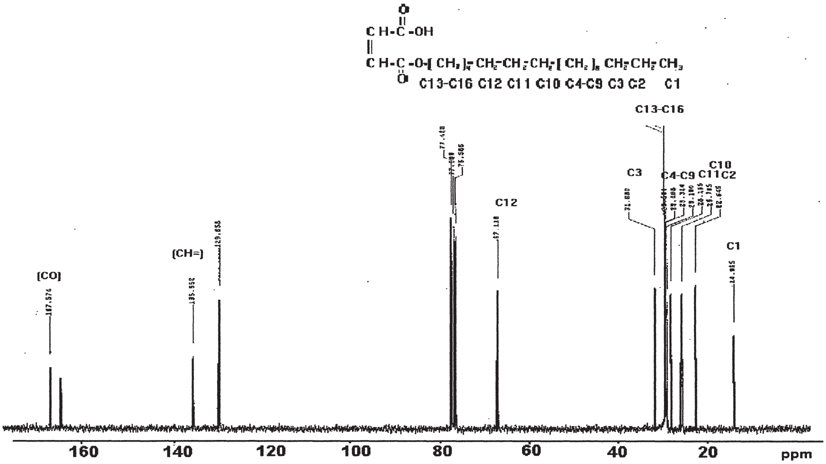

Fig. 3. ^{13}C NMR spectrum of monohexadecyl maleate (MHM). δ ppm: 14.0 (C1), 22.6 (C2), 25.7 (C10), 28.1 (C11), 29.1-29.5 (C4→C9), 29.5-29.6 (C13→C16), 31.8 (C3), 67.1 (C12), 129.0-135.5 (CH=), 165.0 and 167.5 (CO).

Synthesis and characterization of the poly (VAM-co-MAM) copolymers

Copolymers of vinyl acetate (VAM) and monoalkyl maleates (MAM) having butyl (MBM), dodecyl (MDM) and hexadecyl (MHM) alkyl chains, respectively, have been synthesized using either a batch or a semi-continuous addition process of vinyl acetate. The results are reported in Table 3 and Table 4. A typical NMR spectrum of the copolymers is given in Fig. 4.

Table 3. Effect of the feed composition and of the addition process of vinyl acetate on the Tg of the copolymers.

			Feed composition		Copolymers		
Process		**Copolymers**	**VAM (wt%)**	**MAM (wt%)**	**MAM (wt%)[a]**	**Tg (°C)**	**Conv. (%)**
Batch	1	poly(VAM)	100	0	0	36	98.9
	2	poly(VAM-co-MBM)	67	33	31	40	95.4
	3	poly(VAM-co-MDM)	95	5	4	40	98.3
	4	poly(VAM-co-MDM)	90	10	-	40	88.5
	5	poly(VAM-co-MHM)	95	5	4	40	94.1
	6	poly(VAM-co-MHM)	90	10	-	40	98.0
Semi-continuous	7	poly(VAM-co-MBM)	80	20	-	25	97.2
	8	poly(VAM-co-MDM)	80	20	-	32	99.0
	9	poly(VAM-co-HDM)	95	5	-	32	99.8

[a] Determined by ^1H NMR analysis of the copolymers.

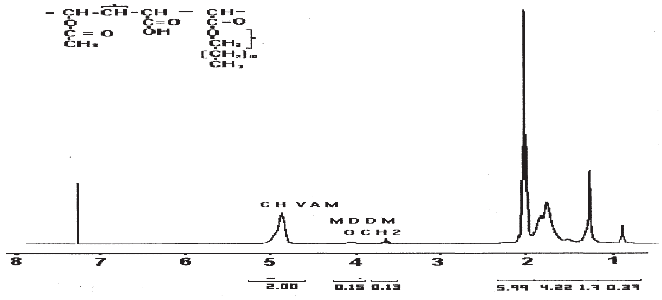

Fig. 4. ^1H NMR spectrum of the copolymer **poly(VAM-co-MDM).** δ ppm: 5.35 (2H, CH) vinyl acetate; 4.35 (2H, OCH_2) monododecyl maleate.

The results in Table 3 show that the weight fraction of monoalkyl maleates in the copolymers, determined by proton NMR analysis, is very similar to the feed composition. This proves that the monoalkyl maleates have reacted and have been, consequently, incorporated in poly(vinyl acetate-co-monoalkyl maleate) copolymers since they cannot homopolymerize. High conversions of the copolymers are obtained under the conditions given in Table 3. However, in the batch experiments, the monoalkyl maleates incorporated in the latex particles did not contribute, as expected, to a significant decrease of the Tg of the copolymers. Internal plastification of poly(vinyl acetate) using monoalkyl maleates comonomers, was achieved only by using a semi-continuous addition process of vinyl acetate. We show that monobutyl maleate gives the best results in our experimental conditions with a decrease of the Tg from 36°C to 25°C (see Table 3). However, it is worthwhile to notice that the monododecyl maleate, introduced at very low concentrations, also provides somewhat a decrease of the Tg of the copolymers. Indeed, it was expected that the higher the chain length of the hemiesters, the larger the decrease of the glass transition temperature of the copolymers. Such a plasticizing effect could be very interesting in several applications since it would be then possible to significantly decrease the amount of functional monomers in the latexes.

Table 4. Molecular weights and molecular weight distributions of the copolymers obtained in batch.

	Copolymers	**Wt % of MAM in the feed**	**Mn x 10^3**	**Mw x 10^3**	**Mw/Mn**
1	poly(VAM)	0	168	610	3.62
2	poly(VAM-co-MBM)	33	108	464	4.23
10	poly(VAM-co-MBM)	45	51	142	2.75
3	poly(VAM-co-MDM)	5	995	1617	1.62
4	poly(VAM-co-MDM)	10	281	905	3.21
5	poly(VAM-co-MHM)	5	639	1396	2.18
6	poly(VAM-co-MHM)	10	86	760	2.92

The results of Table 4 indicate that the molecular weights of the copolymers are much different from the molecular weights of pure poly(vinyl acetate). We can observe that the monoalkyl maleates contribute to a decrease of the molecular weights. The higher the amount of hemister in the copolymers, the lower are the molecular weights. This decrease can be attributed to the formation of some hydrosolubles polymers formed in the aqueous phase. In order to give further insights in the locus of polymerization of the monoalkyl maleate, it was then decided to separate by centrifugation (15 000 rpm for 2 hours) the poly(VAM-co-MDM) latex particles from the aqueous phase and to analyze individually the serum and the polymer particles by ^{1}H NMR spectroscopy.

Table 5. Characterization of the copolymer (sample 8 in Table 3) after separation by centrifugation of the aqueous phase (serum) from the latex particles.

	Feed	**Copolymer**				
	MDM (wt%)	**MDM (wt%)**[a]	**Tg (°C)**	**Mn x 10^3**	**Mw x 10^3**	**Mw/Mn**
Latex particles	20	7	36	116	779	6.6
Serum	20	28	21	96	406	4.2

[a] Determined by ^{1}H NMR analysis.

The results in Table 5 indicate that the serum contains a larger amount of monoalkyl maleate than the polymer in the particles. Indeed, the copolymer in the serum contains 28wt% of monoalkyl maleate while the amount of monoalkyl maleate in the polymer particles does not exceed 7 wt%. In addition, the amount of MDM in the serum is larger than the concentration of monoalkyl maleate in the feed. This proves that the serum contains copolymers enriched in monododecyl maleate while on the opposite, the latex particles are essentially made of poly(vinyl acetate) and does not contain a large quantity of hemiester. As a matter of fact, the Tg of the copolymer in the serum (21°C, see Table 5) is significantly lower than the Tg of poly(vinyl acetate) (36°C, see Table 3), while the Tg of the copolymer in the latex particles precisely corresponds to the Tg of pure poly(vinyl acetate).

Conclusions

In the present study, monoalkyl maleates functional monomers have been synthesized and successfully copolymerized with vinyl acetate. We showed that adding vinyl acetate very slowly, i.e. semi-continuously, could control the microstructure of the copolymers. This procedure allows synthesizing copolymers rich in monoalkyl maleates, which contributes to a decrease of the glass transition temperature of the polymer particles.

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References

1. A. Brar, S. Charan, *J. Appl. Polym. Sci.* **53**, 1813 (1994)
2. A. Brar, Sunita, *Eur. Polym. J.* **27**, 17. (1991)
3. L. Wilson, *PDC magazine*. **2**, 2 (1996)
4. H. Chen, Y. Wu, Z. Jin, *J. Appl. Polym. Sci.* **41**, 427 (1994)
5. A. Zicmanis, T. Hamaide, A. Guyot, *Colloid Polym Sci.* **275**,1 (1997)