Latex Sequence Distribution Determination by Pyrolysis-Capillary Gas Chromatography-Mass Spectrometry

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SUMMARY: Physical properties of latex films depend on how the monomers are distributed along the polymer chain.The monomer sequence distribution is traditionally measured by ^{13}C nuclear magnetic resonance (^{13}C NMR). However, spectral interpretation is difficult, especially when more than 2 monomers are used. Pyrolysis/capillary gas chromatography/mass spectrometry (PGC/MS) is a faster and more resolutive technique, giving detailed informations on the degraded volatiles chemical nature, the polymer monomer composition and sequence distribution. In this paper, styrene-ethyl acrylate (50/50 molar ratio) latexes, prepared by batch, semi-batch, power-feed and core-shell emulsion polymerization were investigated. We compared the sequence distribution results measured by PGC/MS, with calculated values obtained through an emulsion colymerization kinetic model. PGC/MS was used to follow the polymer sequence distribution during polymerization. This analytical tool may therefore be used as a high resolution chemical sensor for on-line latex polymerization.

Introduction

Industrial polymer latexes made through radical emulsion polymerization are used as binders in textile, paper, paint and adhesive formulations. The monomer distribution along the high molecular weight polymer chains is an important parameter which determines the mechanical properties of latex films. With a good control of monomer incorporation, one can prepare latexes possessing remarkable film properties.

Nuclear magnetic resonance (^{13}C NMR) is certainly the most known analytical tool for polymer microstructure investigation. Sequence distribution of styrene-acrylic latexes has been investigated by NMR[1-2]. However, the technique is time consuming and is hardly used for systems dealing with more than 2 monomers. The reason is that NMR resonance chemical shifts are affected by the homopolymer and copolymer microstructures (tacticity and

cotacticity), leading to complex spectra hard to interpret by non experts. Numerical simulation using polymerization kinetic models[3-5] is an alternative tool to calculate latex microstructure and thermal or mechanical properties like glass transition temperature or dynamic mechanical properties[6]. Pyrolysis/gas chromatography (PGC) is a common tool for polymer chemists. Numerous natural and synthetic polymers have been characterized by PGC[7]. The success of PGC is due to reliable pyrolytic technologies, high resolution capillary GC and the coupling of GC with mass spectrometry (MS).or Fourier-transformed infrared spectroscopy (FTIR) for molecular identification of evolved volatiles. PGC/MS was used to validate the degradation mechanism of polymers[8] and especially polyacrylics[9-10]. Microstructure investigation of these polymers was described in literature[11-13]. The quantitative approach of polymer microstructure using the concept of boundary effects was proposed[14-16].

Experimental

Analytical methods PGC/MS : One microliter of latex (25 % solids) was layered on the Pyroprobe 170 (CDS) platinum lamellae. Sample was rapidly heated to 600°C within 20 milliseconds. Degradation products were separated on a SE 52, 25 m x 0.25 mm I.D capillary column. It was heated from 40 °C to 300°C (5 °C/min) and purged with helium at 100 ml/min. The HRGC 5300 GC was equipped with an FID detector, and full molecule identification was realized by mass detection (Finnigan ITD) in the EI and CI modes.

^{13}C NMR : ^{13}C NMR spectra from mixtures of latex-D,acetone 1/1 vol. were measured with a AC 200 Brucker spectrometer (operating conditions : 10 mm tube at 50°C, IA 30°, AD 2s, AT 0.737 s, 2000 scans, deconvolution software LIMSI).

Differential scanning calorimetry (DSC) : Latex films were scanned from -50°C to 150°C at 5°C/min (Mettler DSC 30). Tg (inflection point method) and transition domain (ΔTg) were recorded.

Particle size (Dp): The hydrodynamic particle size Dz and distribution index Ip of diluted and filtered latexes were recorded (Malvern Zetamaster)

Numerical simulation. A home-made sotfware (SIMPOLY) was used to calculate the polymer sequence distribution, chemical composition and glass transitions during conversion. It can handle up to 7 monomers when using batch,semi-batch, power-feed or core-shell processes. Data such as chemical composition (S/AE 50/50 mole ratio), reactivity ratios (r1$_{S/AE}$ = 0.8 ; r2$_{AE/S}$ = 0.25), monomer partition coefficients in the aqueous and organic phases,

monomer/polymer swelling ratio, monomer feed conditions, homopolymer glass transition temperatures are needed for the model used.

Latex synthesis Four styrene-ethyl acrylate S/AE 50/50 mole ratio, 45 % solids latexes were prepared through batch, semi-batch, power-feed et core-shell polymerization (B(S/AE), SB(S/AE), PF(S/AE) and CS(S/AE)). Microstructure differences are expected to be found when modifying the process. Two complementary S/AE 20/80 and 80/20 mole ratios, 40% solids, were batch polymerized. They were used for quantitative composition analysis. Details of the recipe are not described in this paper.

Results and Discussion

Physical characteristics of latexes (Tab. 1). The high solids latexes were monodisperse in size and showed significant differences in glass transition temperatures (Tg) and transition domains (ΔTg), although having the same chemical composition, S/AE 50/50 mole ratio . The **B*(S/AE)*, SB*(S/AE)* latexes gave homogeneous films with well defined Tg's, whose values are intermediate between the homopolymer values (Tg (S) :104°C and Tg(AE) :-18°C). The **PF*(S/AE)* latex gave a complex structure, with ΔTg spread over 100°C and Tg unclearly defined. The **CS*(S/AE)* latex possessed 2 Tg having the same values of the S and AE homopolymers.

Table 1. Latex characteristics

Properties	Batch	Semi-batch	Power feed	Core-shell
Solids content (%)	45	45	45	45
Particle size Dz (nm) *	85	118	100	140
Tg / ΔTg (°C) **	42/18	40/10	62/96	-16/10 and 100/10
Tg / ΔTg (°C) ***	40/25	40/14	60/90	-18/10 and 100/10

* DLS Malvern ** DSC Mettler (3°C/min) *** kinetic modeling

These differences are expected if one considers the Johnston's equation 1 and takes into account the importance of sequence distribution in the copolymer Tg values[5]

$$1/Tg = [Wa.Paa/Tg(a)] + [Wb.Pbb/Tg(b)] + [(Wa.Pab + Wb.Pba)/Tg (ab)] \qquad (1)$$
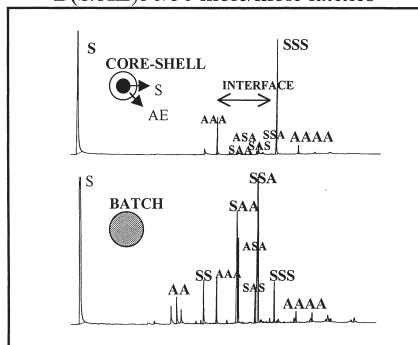*Tg(i) : homopolymer (i)Tg ; Tg(ij) : alternated copolymer (ij) Tg*
Pij : probability having dyad (ij) ; W(i) : mass content of monomer (i).

The numeric simulation gave identical results of Tg and ΔTg for the 4 latexes, validating therefore the kinetic model used by our software (Tab. 1)

Copolymer Pyrolysis

Flash pyrolysis of polymers results in complex mixtures of monomers, oligomers and other volatiles formed by depropagation reactions, intra and intermolecular transfer followed by β-scission, recombination, oxidation, ring formation, dehydrogenation, and elimination reactions[7]. Preliminary work showed that S and AE homopolymers were completely degraded at 600°C, the volatiles formed are essentially monomers (70%) and oligomers (30%). Trimers were the main oligomers formed, although a small amount of dimers and tetramers were also detected Copolymers S-AE gave similar informations except that hybrid trimers are formed instead of homo trimer. We can therefore use the trimers centered on S (SSS, SSA, ASA) or A (AAA, AAS, SAS).to evaluate the process influence on microstructure. The PGC chromatograms of **CS***(S/AE)* and **B***(S/AE)* latexes are chosen to illustrate the idea (Fig. 1). We found mainly homo triads AAA and SSS for the **CS***(S/AE)* latex. However, small peaks of hybrid triads were detected, corresponding to the core-shell interphase. In the contrary, we found for the **B***(S/AE)* latex a majority of hybrid triads and little homo triads. We also have found that all the triads of a S/AE/methyl methacrylate terpolymer are fully separated and identified using PGC. Let's see now how quantitative results could be obtained.

Fig1 Pyrolysis chromatograms of **CS(S/AE)** and **B(S/AE)**50/50 mole/mole latexes

Chemical Composition

Polymer composition are traditionally measured using NMR, FTIR or elemental analysis. PGC had been used to do so, on the basis of evolved monomer calibration[10]. In this paper, we showed that microstructure data obtained with PGC could also be used for chemical composition quantification. In order to demonstrate it, we analyzed successively the three **B***(S/AE)* 20/80, 50/50, 80/20. We found a linear relationship between the ratio Σ(triads S

Fig. 2 PGC Calibration curve for latex composition quantification (triads ratio (S/AE) vs. monomer ratio (S/AE)- Latex B(S/AE) : 20/80, 50/50, 80/20 mole/mole)
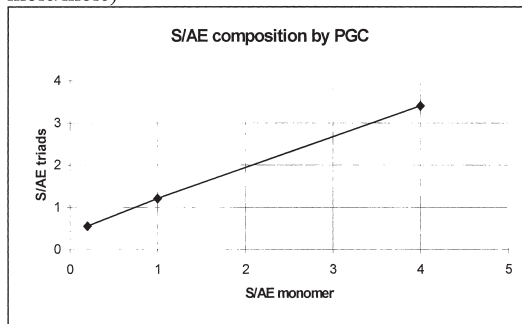
centered)/Σ (triads A centered) to the ratio S/AE monomer (Fig.2). It is then straightforward to access to polymer composition at any moment

Microstructure

PGC, as said before, gives detailed informations on the S/AE latex microsructrure. If qualitative information are just needed, the triads surface area percentage can directly be used to compare the effect of processes on microstructure. However, if PGC is to be compared to other techniques such as NMR or kinetic modeling, data treatment needs to be performed. The reasons for it are a) FID detection changes from the carbon content of each molecule, b) formation kinetics of each triad depends on its initial surroundings, in another terms, on the probability of formation of initial pentads (boundary effects[13,14]).

Y(AAA)   = Kd * P(AAA)

with   **Kd = kd1 Pb(AAAAA) + 2.kd2 .Pb(AAAAB) + kd3.Pb(BAAAB)**

Y (AAA) :   AAA triad fraction measured by PGC
kdi   :   formation constant of triads from pentads
P(AAAAA) : probability of AAAAA pentad formation

After several unsuccessful attempts to solve the problem, we have decided to determine empirically a corrected FID response for each measured triad. The following method was adopted. Triads of the three B*(S/AE)*, SB*(S/AE)*, PF*(S/AE)* S/AE 50/50 mole ratio latexes were measured by PGC, ^{13}C NMR and kinetic modeling. We have attributed to each PGC triad surface peak a correction factor so that results between PGC and NMR are best fitted for the three latexes. We obtained therefore the FID mean coefficient for each triad : K_{AAA} =1 K_{AAS} =0.8 ; K_{SAS}=2.8 ; K_{ASA}=1.5 ; K_{SSA}=0.5 ; K_{SSS} =1 . Comparative results between PGC, NMR and kinetic modeling are listed in Table 2.

We can now proceed on quantitative comparison of the latex fabrication process on sequence distribution. Results for the B*(S/AE)*, SB*(S/AE)*, PF*(S/AE)* and CS*(S/AE)* latexes are shown in Fig 3

Table 2. Sequence distribution - Latex B(S/AE) 50/50 mole/mole 100% conversion

	AAA	AAS	SAS	ASA	SSA	SSS
Pyrolysis/GC	8	21	22	14	22	9
^{13}C NMR	8	20	24	18	24	6
Kinetic model	7	18	23	21	23	7

Fig. 3   PGC sequence distribution of B(S/AE), SB(S/AE), PF(S/AE) and CS(S/AE) 50/50 mole/mole latexes
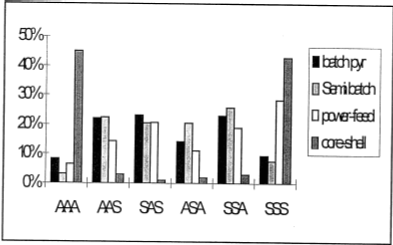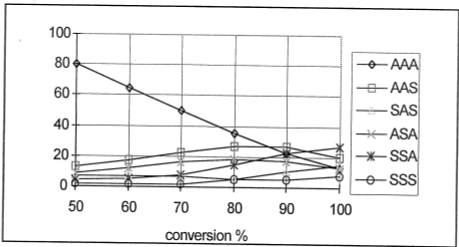
Fig. 4 Kinetics of sequence formation during polymerization. Power-feed latex (PF S/AE), 50/50 mole/mole

As expected, the core-shell latex contained large fractions of SSS triads from the styrene core and AAA triads from the acrylic shell. Its interphase composition was described by small fractions of hybrid triads AAS, SAS, ASA, SSA. Batch and semi-batch latexes possessed mainly hybrid triads and gave homogeneous copolymers. The structure of the power-feed latex is more complex, possessing significant SSS triads, therefore long sequences of styrene, along with hybrid triads . These microstructure differences are on the origin of the different temperature transitions Tg and ΔTg we discussed in the beginning.

Sequence formation kinetics

Consequently to this preliminary work, we have now a powerful and unique tool to experimentally follow triad formation during polymerization. Pipetted samples are analyzed by PGC in about 30 minutes each. The case of power-feed polymerization is shown in Figure 4 just as an example of what information we can get. PGC could therefore be considered as a new chemical sensor for studying polymer kinetics.

Conclusion

The hybrid technique pyrolysis/capillary gas chromatography/mass spectrometry (PGC/MS) was used in this paper to characterize styrene-ethyl acrylate (S/AE) latexes. The volatiles formed by a thermal degradative process are mainly monomers and trimers (triads). The observed triads reflect the microstructure of the original polymer and directly influence final film properties such as phase compatibility, thermal properties and mechanical properties . We showed that the sequence distributions of latexes made by batch, semi-batch, power-feed and core shell emulsion polymerization were very different from one another and are the source of differences in glass transition temperatures of the latex films. Furthermore, we showed that composition quantitative analysis could be done with the microstructure data as well as following detailed triad formation kinetics during polymerization. Results of microstructure are coherent when compared to other techniques like C_{13} NMR or kinetics modeling.

PGC/MS is also a high resolution technique capable of handling more than 2 monomers and could therefore be considered as an unique and powerful tool for latex characterization, for following polymer microstructure kinetics and for process optimization.

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