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Synthesis of Poly(vinyl acetate)-*block*-poly(dimethylsiloxane)-*block*-poly(vinyl acetate) Copolymers by Iodine Transfer Photopolymerization in Miniemulsion

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Summary: Iodine transfer polymerization of vinyl acetate in aqueous miniemulsion, initiated by UV radiation in the presence of an α,ω-diiodo-poly(dimethylsiloxane) macrophotoiniferter has been performed. The formation of a triblock copolymer latex PVAc-*b*-PDMS-*b*-PVAc has been evidenced by ^{1}H-NMR and size exclusion chromatography. The size of the PDMS and PVAc blocks were modulated thus opening the way to a wide range of copolymers with different properties. A detailed study of the reaction mechanism showed the importance of the aqueous dispersed medium to achieve a controlled polymerization.

Keywords: block copolymers; iodine transfer polymerization; miniemulsion; photopolymerization; poly(dimethylsiloxane); poly(vinyl acetate)

Introduction

Novel macromolecular architectures, like block, graft or star copolymers combine the properties of two different polymers, thus opening the way to novel high-tech applications. Innovative amphiphilic poly(vinyl alcohol)-poly(dimethylsiloxane) copolymers can be synthesized by the controlled hydrolysis of the vinyl acetate blocks in poly(vinyl acetate)-poly(dimethylsiloxane) (PVAc-PDMS) copolymers.[1–3] Potential applications of PVAc-based copolymers include coatings and adhesives.[4,5] The incorporation of PDMS blocks in the structure would enhance PVAc properties like flexibility and resistance to moisture. In spite of these potential applications, these copolymers have not been widely studied yet. One of the methods of synthesis of such PVAc-PDMS copolymers consists in the use of conventional radical polymerization (with a PDMS macro-azoinitiator[6] or macro-peroxyinitiator[7]). Tezuka et al.[1] used a coupling reaction between poly (vinyl acetate) containing chlorosilyl end groups and PDMS containing NaOSi end groups. Several studies deal with the copolymerization of a PDMS macromonomer (with dimethylvinylsilyl end group) and vinyl acetate to form graft copolymers.[2,3]

Controlled radical polymerization (CRP)[8] has emerged in recent years as a powerful and simple technique for the synthesis of well-defined polymers and novel functional materials. Destarac et al.[9] claimed the use of controlled radical polymerization (MADIX)[10] to synthesize PVAc-*b*-PDMS-*b*-PVAc triblock copolymers. Several groups have polymerized vinyl acetate by iodine transfer polymerization (ITP).[11–15] Our group used an α,ω-diiodo poly(dimethylsiloxane) (**$\underline{1}$**) (Scheme 1) to synthesize PVAc-*b*-PDMS-*b*-PVAc triblock copolymers by iodine transfer polymerization in bulk at

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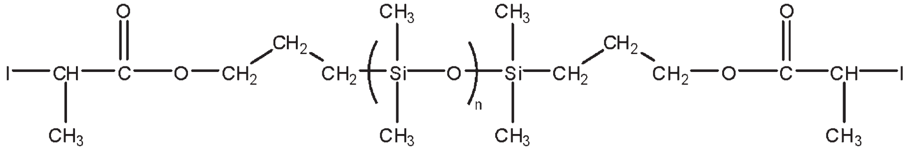


(1)

Scheme 1.
α,ω-diiodo poly(dimethylsiloxane) (1).

80 °C.[15] The molecular weight evolution proved the controlled character of the synthesis; high conversions around 75% were obtained. However, reproducibility was scarce unless important cautiousness was applied. Moreover, the PVAc-I chain-end is prone to degradation (Scheme 2)[11] and thus milder conditions of polymerization would be preferable.

In this work we studied the polymerization of vinyl acetate at room temperature in the presence of an iodinated macrophotoiniferter to make PVAc-*b*-PDMS-*b*-PVAc triblock copolymers in miniemulsion. To our knowledge, it is the first time that vinyl acetate is polymerized in the presence of a photoiniferter in dispersed aqueous medium.

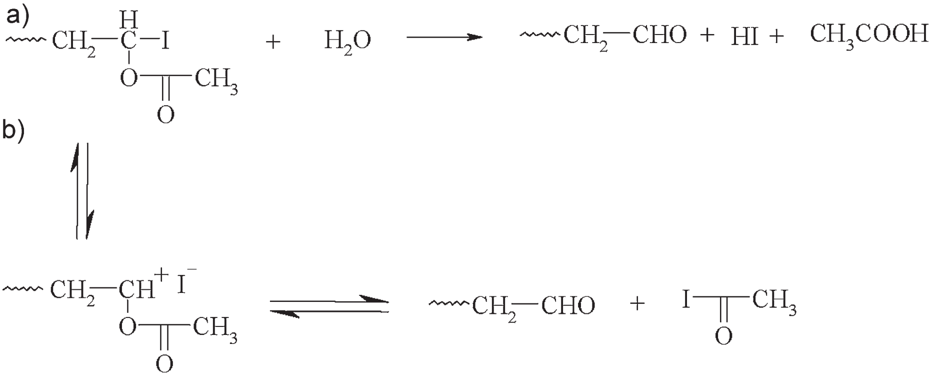
Experimental Part

Materials

For the synthesis of the α,ω-diiodo poly(dimethylsiloxane), see our previous publication on the synthesis of PS-*b*-PDMS-*b*-PS triblock copolymers by ITP in miniemulsion polymerization.[16] Vinyl acetate (VAc, Acros, 99%) was purified by vacuum distillation before use. Mersolat H40 (sodium alkane sulfonate surfactant, Lanxess, 40% aqueous solution), octamethylcyclotetrasiloxane (D4, Shin Etsu, > 98%) and Tonsil EX0096 (Diatomee clay modified with sulfonic acid, Süd Chemie) were used as received. 2,2′-Azobisisobutyronitrile (AIBN, Fluka, 98%) was purified by recrystallization from methanol. Water was de-ionized by passing through columns packed with ion exchange resins.

General Procedure for Polymerisation

Typically the macro-transfer agent I-PDMS-I (1) (0.24 g, $M_{n,SEC} = 1340\ g \cdot mol^{-1}$, PDI = 1.6, 0.18 mmol) dissolved in vinyl acetate (3.75 g, $M = 86.09\ g \cdot mol^{-1}$, 43.6 mmol) was placed in a 50-mL glass reactor. After three freeze-thaw pump cycles, a degassed solution of Mersolat H40 (0.5 g of a 40%



Scheme 2.
Hydrolysis (a) and decomposition (b) of iodo end groups of poly(vinyl acetate) after and/or during iodine transfer polymerization.

aqueous solution) in water (25 g) was added. Then the solution was miniemulsified by sonication (Bioblock Scientific Vibra Cell 75043, 30 s, 8 kHz) under argon flow at 0 °C. No further argon purging was performed in order to avoid monomer stripping and the reaction was conducted at room temperature under UV radiation using a Philips HPK 125W 4A lamp (2.5 mW.cm^{-2}), with magnetic stirring for 16 h. Samples were withdrawn with a syringe at regular intervals. Conversion was determined by gravimetric analysis. Polymerization time 16 h, vinyl acetate conversion 82%, theoretical number-average molecular weight $M_{n,th} = 18\,500\ g \cdot mol^{-1}$, number-average molecular weight determined by size exclusion chromatography $M_{n,SEC} = 19\,200\ g \cdot mol^{-1}$, number-average molecular weight determined by ^{1}H NMR $M_{n,NMR} = 19\,100\ g \cdot mol^{-1}$, polydispersity index PDI = 2.31, particle diameter D_p = 160 nm (unimodal particle size distribution).

General Procedure for Poly(dimethylsiloxane) Chain Extension

Octamethylcyclotetrasiloxane (D4, 20.3 g, $M = 294\ g \cdot mol^{-1}$, 69 mmol) and the macro-transfer agent I-PDMS-I (**1**, 1.47 g, 1.1 mmol) are introduced in a 250 mL round bottom flask. After stirring for a few seconds to make a homogeneous solution, Tonsil EX0096 (I) (0.203 g, 1 wt.%/D4) is added. The mixture is heated at 80 °C for 48 h in the dark. The polymer is precipitated in methanol to remove the excess of D4. The resulting polymer is dissolved in diethyl ether and filtered to remove the catalyst (Tonsil EX0096 (I)). Diethyl ether is removed under reduced pressure (10^{-2} mbar). $M_{n,targeted} = 19\,800\ g \cdot mol^{-1}$, $M_{n,theoretical} = 18\,900\ g \cdot mol^{-1}$, yield = 95%, $M_{n,NMR} = 20\,100$, $M_{n,SEC} = 18\,000$, PDI = 1.58.

Characterizations

Size exclusion chromatography (SEC) was performed with dried samples dissolved in THF, with a Spectra Physics Instruments SP8810 pump equipped with two 300 mm columns thermostated at 30 °C (columns mixed-C PL-gel 5 μm from Polymer Laboratories, 2×10^2–2×10^6 MW range) and a Shodex Rise-61 refractometer detector. THF was used as eluent at a flow rate of 1.0 mL.min^{-1}. Calibration was performed with polystyrene standards from Polymer Laboratories. ^{1}H NMR analyses were performed in $CDCl_3$ on a Bruker Avance 250 MHz. Particle size of the latex was determined with a Nanotrac 250 particle analyzer (Microtrac Inc.). pH measurements were performed with a Consort P500 apparatus from Bioblock Scientific. Iodide concentrations $[I^-]$ were measured with a PHM 210 standard pH meter from Radiometer Analytical with an iodide-selective electrode ISE25I-9 and a reference electrode REF201 from Radiometer Analytical.

Discussion

The fragility of the poly(vinyl acetate)-iodinated chain-ends is a major obstacle to the controlled polymerization of vinyl acetate by iodine transfer polymerization in aqueous dispersed media. In order to decompose the radical initiator, high temperatures are required which accelerate the chain-end degradation.[15] In order to obtain conditions where chain-ends are stable enough to allow the synthesis of controlled polymer blocks in aqueous dispersed media, the reaction temperature must be decreased. For this purpose we initiated the polymerization under UV radiation at room temperature (photo-activation instead of thermal activation).

In miniemulsion polymerization, the monomer droplets are formed by sonication of the initial monomer-in-water emulsion. To increase the stability of these monomer droplets and to avoid Ostwald ripening, a hydrophobic agent such as *n*-hexadecane is usually added.[17] In our study, however, this was not necessary because the PDMS transfer macro-transfer agent (**1**) plays the dual role of the hydrophobe and macro-transfer agent.

Table 1.
Effect of transfer agent concentration on miniemulsion polymerization of vinyl acetate[a].

Run	VAc/AIBN/PDMS (mol/mol/mol)	Theoretical solid content (%)	$M_{\text{transfer agent}}$ ($g \cdot mol^{-1}$)	Time (h)	Conv. (%)[b]	$M_{n,th}$[c] ($g \cdot mol^{-1}$)	$M_{n,SEC}$ ($g \cdot mol^{-1}$)	PDI	$M_{n,NMR}$ ($g \cdot mol^{-1}$)	pH	d_p (nm)[d]
1	232/0.11/1	15	1 340	7	78	17 100	13 700	2.24	17 200	1.97	163
2	115/0/1	9	1 340	15	67	8 000	9 100	2.18	8 400	1.94	305
3	243/0/1	14	1 340	16	82	18 500	19 200	2.31	19 100	1.88	160
4	367/0/1	11	1 340	16	95	31 400	31 500	2.50	34 000	2.28	260
5	313/0/1	13.5	20 100	15	86	43 300	45 600	2.20	44 400	2.30	360

[a] under UV radiation with [Mersolat H40] = 8 g.L^{-1};
[b] conversion determined by gravimetry;
[c] $M_{n,\text{theoretical}} = (\text{mass of monomer}) \times (\text{monomer conversion})/(n_{\text{PDMS}}) + M_{\text{transfer agent}}$;
[d] d_p: particle diameter.

In all the experiments (Table 1), a low pH (around pH = 2) resulted due to the competitive chain-end degradation by HI formation (Scheme 2). The PVAc-I chain-ends are unstable and undergo relatively fast degradation. However, under photopolymerization conditions in miniemulsion, they are stable enough to allow the synthesis of the desired triblock copolymer, whose theoretical molecular weight is given by Equation (1).

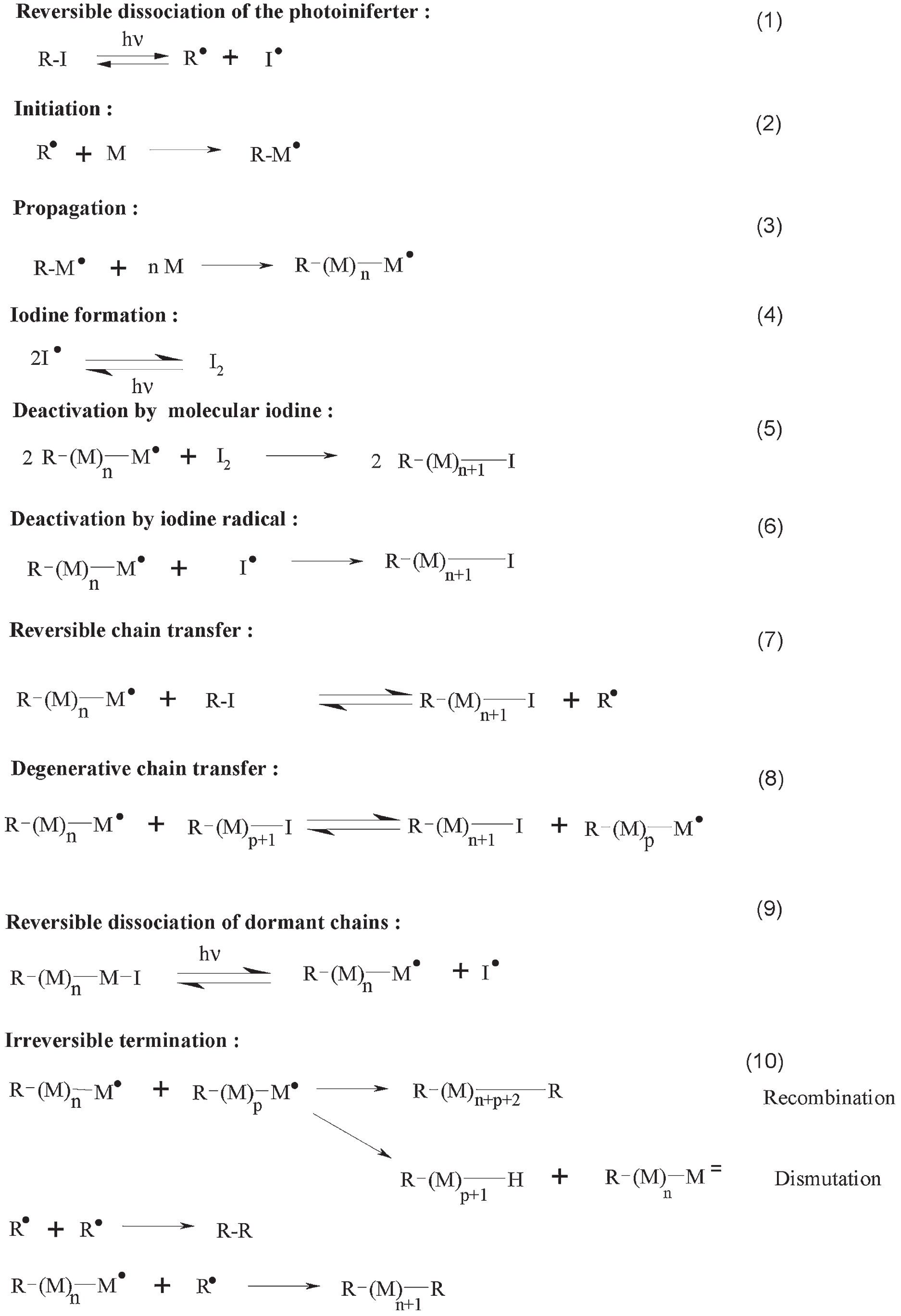
$$M_{n,\text{theoretical}} = M_{n,(1)} + \frac{m_{\text{vinyl acetate}}}{n_{(1)}} \times \alpha_{\text{vinyl acetate}} \qquad (1)$$

in which $M_{n,(1)}$ is the mean number average molecular weight of (**1**), $m_{\text{vinyl acetate}}$ is the mass of vinyl acetate, $n_{(1)}$ is the number of moles of **1** and $\alpha_{\text{vinyl acetate}}$ is the conversion of vinyl acetate.

In the first experiment under UV radiation (Table 1, run 1), a small amount of 2,2′-azobisisobutyronitrile (AIBN) was used as radical initiator. A stable white latex with a high monomer conversion (around 80%) was obtained in 7 h. The experimental molecular weight by SEC was slightly lower than the expected theoretical molecular weight given by Equation (1). This could be due to the formation of a small amount of homo(PVAc) initiated by the radical initiator (AIBN). A relatively high polydispersity index of 2.24 was obtained. The desired triblock copolymer structure was evidenced by ^{1}H NMR and SEC analyses.

In all the other experiments (Table 1, runs 2–5), we took advantage of lability of the C–I bond under UV radiation to perform the polymerization in the absence of the added azo-initiator, which could lead to pure triblock copolymers without homopolymer formation. The same experiment as run 1 but without the addition of AIBN (Table 1, run 3) gave very promising results: a stable white latex with a good control over the molecular weight and a high monomer conversion was obtained in 16 h. Since no radical azo-initiator was added, the initiation of the polymerization was due to the homolytic scission of the C–I bond of macrophotoiniferter (**1**) under UV radiation (Scheme 3, step 1). The formed radical propagates by addition of monomer units (Scheme 3, steps 2 and 3). The iodine radical atom recombines with another iodine radical atom to form iodine[18,19] (Scheme 3, step 4) or with a propagating radical[19,20] to form a dormant chain (Scheme 3, step 6). The propagating radical can react with either the iniferter by transfer reaction (Scheme 3, step 7), with dormant chains by degenerative chain transfer (Scheme 3, step 8) or by deactivation with an iodine atom (Scheme 3, step 6) or molecular iodine I_2 (Scheme 3, step 5).[20–24] The dormant chains can also reversibly dissociate under UV radiation (Scheme 3, step 9). Last, propagating radicals can undergo irreversible termination reactions (Scheme 3, step 10).

^{1}H NMR analysis (Table 1, run 3) shows the complete disappearance of the signal



Scheme 3.
Mechanism of radical photopolymerization in the presence of an iodinated photoiniferter.

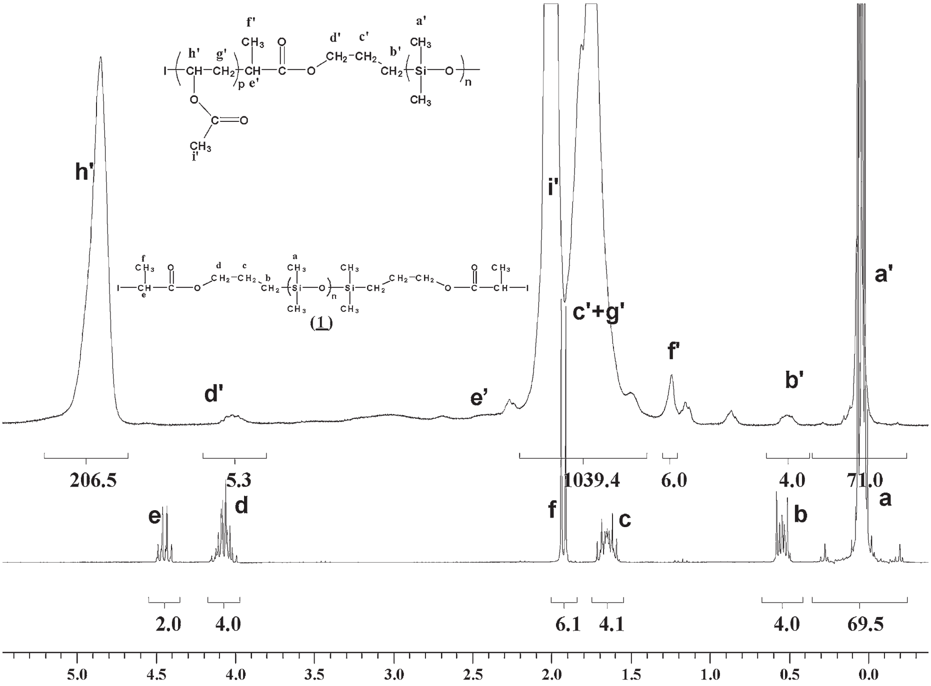


Figure 1.

^{1}H-NMR spectrum of the macrophotoiniferter (**1**) and the triblock copolymer PVAc-*b*-PDMS-*b*-PVAc (poly(vinyl acetate)-*block*-poly(dimethylsiloxane)-*block*-poly(vinyl acetate)) (Table 1, run 3) in $CDCl_3$: H_a (m, 0.04 ppm), H_b (m, 0.54 ppm), H_c (m, 1.67 ppm), H_f (d, 1.93 ppm), H_d (m, 4.08 ppm), H_e (q, 4.45 ppm), $H_{a'}$ (m, 0.04 ppm), $H_{b'}$ (m, 0.51 ppm), $H_{f'}$ (m, 1.24 ppm), $H_{c'}$ and $H_{g'}$ (m, 1.71 ppm), $H_{i'}$ (s, 2.00 ppm), $H_{e'}$ (m, 2.30 ppm), $H_{d'}$ (m, 4.01 ppm), $H_{h'}$ (m, 4.85 ppm).

corresponding to the iodinated chain-ends of the PDMS macrophotoiniferter (H_e) at 4.45 ppm (Figure 1). This gives additional evidence for the formation of a triblock copolymer. ^{1}H NMR analysis permits to assess the number-average molecular weight by integrating the reference signal of the $-\mathbf{CH_2}-Si$ methylene groups next to the Si atom at 0.46 ppm ($I_{b'}$) and comparing it to the integration of the $CH_2-\mathbf{CH}(OCOMe)-CH_2$ protons of the poly(vinyl acetate) chain at 4.85 ppm ($I_{h'}$) (Equation (2)).

$$M_{n,NMR(b')} = M_{n(1)} + \frac{I_{h'}}{I_{b'}/4} \times M_{\text{vinyl acetate}} \qquad (2)$$

in which $M_{\text{vinyl acetate}}$ is the molecular weight of vinyl acetate.

These integrations give values of $M_{n,NMR(b')} = 19\,100\ g \cdot mol^{-1}$ (Table 1, run 3). This result is very close to the theoretical molecular weight $M_{n,th} = 18\,500\ g \cdot mol^{-1}$ and to the molecular weight determined by SEC, $M_{n,SEC} = 19\,200\ g \cdot mol^{-1}$, confirming the successful synthesis of the desired triblock copolymer.

In order to show the controlled character of the polymerization, different PVAc molecular weights were targeted (Table 1, runs 2–4). In all cases, correct monomer conversions and a good correlation between experimental and theoretical molecular weights were observed. When the size of the poly(vinyl acetate) block increases, the polydispersity index increases slightly, presumably due to the increasing formation of dead chains during the polymerization (competition between CRP and chain-end degradation). However, the molecular weight distribution is clearly shifted towards higher molecular weights

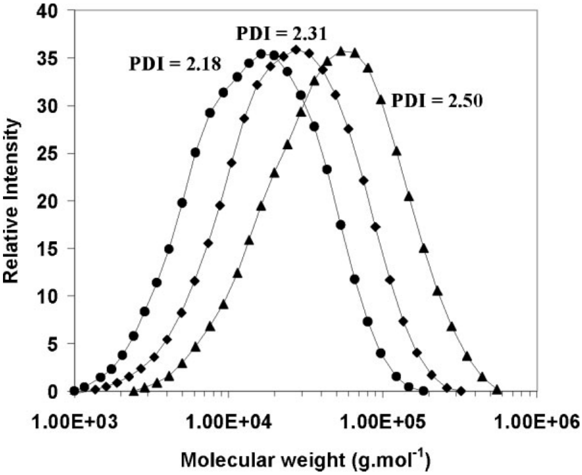


Figure 2.
Molecular weight distributions of poly(vinyl acetate)-*block*-poly(dimethylsiloxane)-*block*-poly(vinyl acetate) copolymers prepared by iodine transfer polymerization in miniemulsion ($M_{n,macrophotoiniferter} = 1340\ g \cdot mol^{-1}$); Theoretical molecular weights ($g \cdot mol^{-1}$): (●) 8 000, (◆) 18 500, (▲) 31 400.

when a higher-molecular-weight PVAc block is targeted while using the same macrophotoiniferter ($M_n = 1340\ g \cdot mol^{-1}$) (Figure 2). By this method, triblock copolymers of predefined molecular weights are easily obtained. Last, unimodal particle size distributions were obtained in all cases.

In order to gain a better understanding of the polymerization mechanism, a similar experiment was attempted in bulk photopolymerization (the same experiment as run 3 in Table 1). No vinyl acetate conversion was detected after 15 h and the reaction medium turned to the characteristic red colour of iodine. The appearance of molecular iodine I_2 is due to a process similar to the persistent radical effect described by Fisher.[25] As soon as several polymer chains are irreversibly terminated (Scheme 3, step 10), iodine begins to accumulate in the reaction medium (recombination of two iodine radical atoms (Scheme 3, step 4)). Since iodine is a strong radical scavenger, the polymerization is inhibited in the presence of this small amount of iodine.[20,22]

In run 3 (Table 1), the final pH and iodide concentration $[I^-]$ could be well correlated with the initial number of iodinated chain-ends $[H^+]_f \approx [I^-]_f \approx [\text{chain-ends}]_o$. This means that almost all chain-ends have been degraded at the end of the polymerization by the mechanism described in Scheme 2 (the polymerization is not living). Note that the macro-transfer agent is stable and is not degraded under these conditions. So, all initial iodinated chain ends have been activated to form the desired triblock structure. During the formation of this triblock structure, the iodinated chain ends are degraded rather fast, leading to a broadening of the molecular weight distribution. In miniemulsion, like in bulk polymerization, a small amount of iodine is formed. Nevertheless, the high monomer conversions show that the formation of a small amount of iodine does not inhibit the polymerization. In order to explain this peculiar behaviour, a kinetic experiment was performed (Figure 3). The monomer conversion increases rapidly with time during the first hour (50% conversion), then the polymerization kinetics slows down considerably. This decrease in the polymerization rate might be assigned to both the degradation of the labile dormant chain-ends (Scheme 2) and the formation of

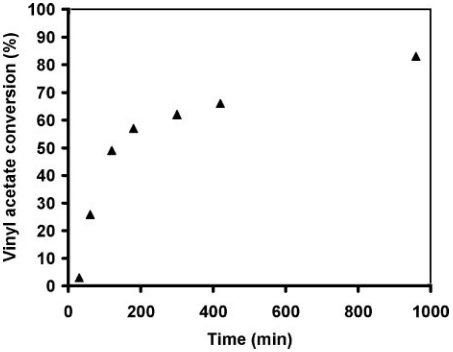


Figure 3.
Evolution of the monomer conversion versus time in the miniemulsion polymerization of vinyl acetate in the presence of a macrophotoiniferter with [Mersolat H40] $= 8$ g.L^{-1}; $M_{\mathrm{macrophotoiniferter}} = 1340$ g $\cdot$ mol^{-1}; targeted molecular weight: 21 700 g $\cdot$ mol^{-1}.

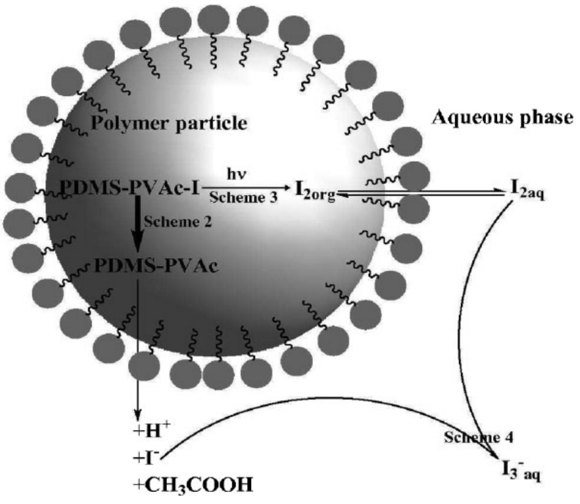
a small amount of iodine (Scheme 3, step 4). However, the formation of iodine should normally completely inhibit the polymerization (as in the bulk experiment). To understand the reason why a rather high monomer conversion can be reached, one has to take into account the complex chemistry of iodine in the aqueous phase (Scheme 4).[26]

The hydrolytic disproportionation of iodine (Scheme 4, equilibrium 1) is negligible in the aqueous phase at 25 °C under UV irradiation (a miniemulsified solution of iodine in ethyl acetate led only to 0.25% of hydrolyzed iodine after 15 h under UV irradiation). In contrast, the complexation of iodide I^- by iodine I_2 to form triiodide I_3^- is a fast equilibrium (Scheme 4, equilibrium 2).[28] The decomposition of the iodinated

$$3\,I_{2,aq} + 3H_2O \overset{K_1}{\rightleftharpoons} IO_3^- + 5\,I^- + 6\,H^+ \qquad (1)$$

$$I_{2,aq} + I^- \overset{K_2}{\rightleftharpoons} I_3^- \qquad (2)$$

Scheme 4.
Iodine hydrolytic disproportionation and triiodide I_3^- formation in the aqueous phase. $K_1 = 2.4 \times 10^{-46}\,\mathrm{mol}^9 \cdot \mathrm{L}^{-9}$; $k_2 = 6.2 \times 10^9\,\mathrm{L} \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$, $k_{-2} = 8.9 \times 10^6\,\mathrm{s}^{-1}$, $K_2 = k_2/k_{-2} = 698\,\mathrm{L} \cdot \mathrm{mol}^{-1}$ at 25 °C with $2 < \mathrm{pH} < 7$.[27,28]



Scheme 5.
Summary of the reactions that make possible the polymerization of vinyl acetate in the presence of an iodinated macrophotoiniferter to proceed in aqueous miniemulsion.

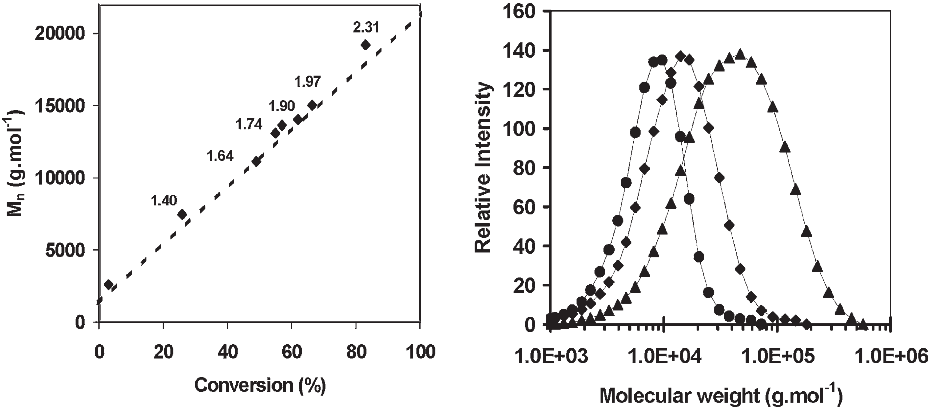


Figure 4.

Miniemulsion polymerization of vinyl acetate in the presence of a macrophotoiniferter with [Mersolat H40] = 8 g.L^{-1}; $M_{macrophotoiniferter}$ = 1340 g · mol^{-1}; targeted molecular weight: 21 700 g · mol^{-1}: Evolution of experimental molecular weight M_n (◆), polydispersity index (labels) and theoretical molecular weight (dotted line) versus monomer conversion; b) Evolution of the molecular weight distribution:(●) conversion 25%, (◆) conversion 49%, (▲) conversion 82%.

chain-ends produces an important quantity of iodide I^- ions (Scheme 2). This aqueous iodide shifts equilibrium (2) nearly completely towards the formation of aqueous triiodide. Therefore the concentration of iodine I_2 in the organic phase becomes negligible, allowing the polymerization to proceed. In summary, the aqueous miniemulsion photopolymerization process is successful because molecular iodine does not accumulate in the organic phase thanks to its reaction with iodide I^- to form aqueous triiode I_3^- (Scheme 5).

For the same kinetic experiment, the experimental molecular weights are very close to the theoretical line (Figure 4a, dotted line). No major deviation of the molecular weights from the theoretical line

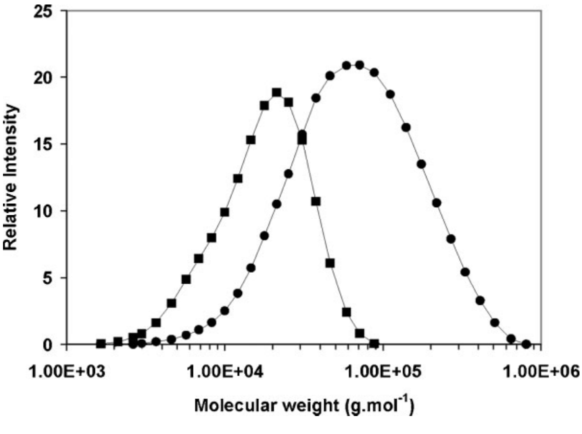


Figure 5.

Molecular weight distributions of high molecular weight ($M_{n,NMR}$ = 20 100, $M_{n,SEC}$ = 18 000 g · mol^{-1}, PDI = 1.58) poly(dimethylsiloxane) (■) and the poly(vinyl acetate)-*block*-poly(dimethylsiloxane)-*block*-poly(vinyl acetate) copolymers prepared by iodine transfer polymerization in miniemulsion under UV radiation ($M_{n,theo}$ = 43 300 g · mol^{-1}, $M_{n,NMR}$ = 44 400 g · mol^{-1}, $M_{n,SEC}$ = 45 600 g · mol^{-1}, PDI = 2.20) (●).

is observed, neither at low conversions, proving that the macrophotoiniferter has a high initiator efficiency, nor at high conversions, showing that, unlike in thermal initiation,[15] transfer to the monomer is negligible. The increase in the polydispersity index with conversion can be assigned to the formation of dead chain-ends as expected from the low stability of the PVAc-I end-groups. Despite the broadening, the molecular weight distribution is shifted towards higher molecular weights as the conversion proceeds (Figure 4b).

Depending on the desired application, it might be advantageous to use a longer PDMS block. A high molecular weight macrophotoiniferter was synthesized by redistribution ($M_n = 20\,100\,\text{g} \cdot \text{mol}^{-1}$) and used in the polymerization of vinyl acetate in miniemulsion under UV radiation (Table 1, run 5). A high monomer conversion of 86% and a good correlation between experimental and theoretical molecular weights were obtained. Furthermore, a clear shift of the molecular weight distribution was observed, indicating that this triblock copolymer synthesis can be successfully performed even with a high molecular weight PDMS macrophotoiniferter (Figure 5).

Conclusion

The synthesis of PVAc-*b*-PDMS-*b*-PVAc copolymers is of major interest because of the possibility of preparing amphiphilic PVA-*b*-PDMS-*b*-PVA triblock copolymers by hydrolysis of the PVAc blocks. So far the synthesis of such copolymers has mostly proceeded by using conventional radical polymerization or coupling reactions. This is only the second time that these triblock copolymers are prepared by controlled radical polymerization and the first time that they are prepared in aqueous dispersed media, which is of major interest for industrial applications. By targeting different molecular weights and performing a kinetic experiment, the controlled character of the polymerization was demonstrated. This synthesis of triblock copolymer does not proceed in the bulk photopolymerization because of the formation of a small amount of iodine I_2 (by a process similar to the persistent radical effect) which behaves as a strong radical scavenger. In contrast, the synthesis is successful in aqueous miniemulsion because the iodide I^-, formed by chain-end degradations, reacts with iodine I_2 to form triiodide I_3^-. This prevents iodine I_2 from accumulating in the organic phase avoiding the inhibition of the polymerization. Promising preliminary tests, which will be reported elsewhere, have been conducted on hydrolysis of the PVAc blocks, directly on the latex.

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