Amphiphilic Polymethacrylate- and Polystyrene-Based Chemical Delivery Systems for Damascones

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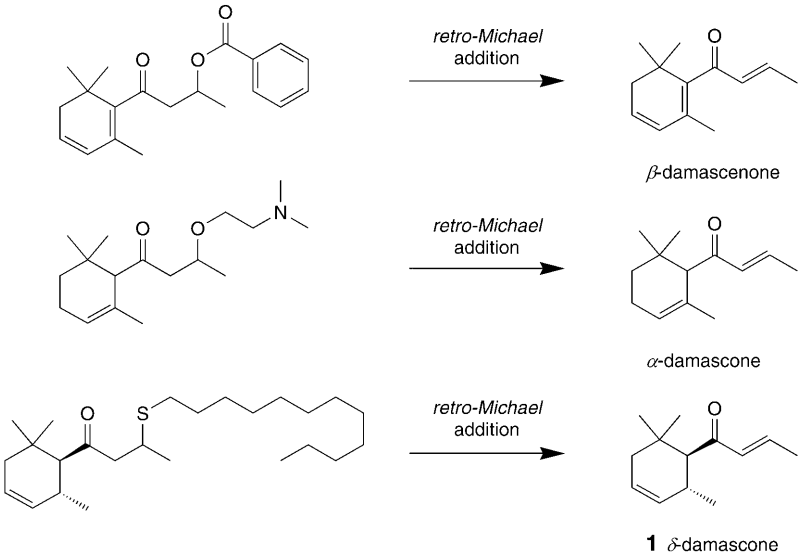
Dedicated to Dr. *Ferdinand Näf* on the occasion of his 65th birthday

Amphiphilic polystyrene- and polymethacrylate-based β-acyloxy ketones were investigated as potential delivery systems for the controlled release of damascones by *retro*-1,4-addition in applications of functional perfumery. A series of random copolymers being composed of the hydrophobic damascone-release unit and a second hydrophilic monomer were obtained by radical polymerization in organic solution by using 2,2′-azobis[2-methylpropanenitrile] (AIBN) as the radical source (*Schemes 2* and *3*). A first evaluation of the polymer conjugates in acidic or alkaline buffered aqueous solution, and in the presence of a surfactant, showed that polymethacrylates and polystyrenes having a carboxylic acid function as hydrophilic group are particularly interesting for the targeted applications (*Table 2*). The release of δ-damascone (**1**) from polymers with poly(methacrylic acid) and poly(vinylbenzoic acid) comonomers in different stoichiometric ratios was thus followed over several days at pH 4, 7, and 9 by comparison of fluorescence probing, solvent extraction, and particle-size measurements (*Tables 3* and *4*). In acidic media, the polymers were found to be stable, and almost no δ-damascone (**1**) was released. In neutral or alkaline solution, where the carboxylic acid functions are deprotonated, the concentration of **1** increased over time. In the case of the polymethacrylates, the fluorescence probing experiments showed an increasing hydrophilicity of the polymer backbone with increasing fragrance release, whereas in the case of the polystyrene support, the hydrophilicity of the environment remained constant. These results suggest that the nature of the polymer backbone may have a stronger influence on the fragrance release than the ratio of hydrophilic and hydrophobic monomers in the polymer chain.

1. Introduction. – The long-lastingness of fragrance perception is often directly associated with the efficiency of perfumed consumer products in body care or household applications. As a consequence of their high volatility, many attempts to control the evaporation of fragrances over time have been undertaken to increase their performance during and after application. As an alternative to encapsulation technologies (see, *e.g.*, [1]), the development of chemical delivery systems for the controlled release of fragrances has become a more and more widely investigated area of research [2]. A series of precursor molecules, so called 'pro-fragrances', have been prepared, and a broad variety of reaction conditions, such as hydrolysis [3][4] or the change of pH [5][6], oxidation [7], the action of temperature, light [8][9], enzymes or microorganisms [10] have been used to trigger the release of perfumery raw materials from their corresponding precursors.

Recently, damascones (=1-(2,6,6-trimethylcyclohexen-1-yl)but-2-en-1-ones) or damascenones (=1-(2,6,6-trimethylcyclohexadien-1-yl)but-2-en-1-ones), the so-called rose ketones [11], were successfully released from different monomeric or dimeric β-amino, β-acyloxy, β-alkoxy, and β-thio ketones (*Scheme 1*) [12] by *retro*-1,4-addition (*retro-Michael*-type reaction, see, *e.g.*, [13]). The good performance of these systems

Scheme 1. *Controlled Release of Rose Ketones from β-Acyloxy, β-Alkoxy, and β-Thioketones by* retro-*1,4-Addition*



in practical applications [14][15] prompted us to investigate the influence of the substrate of the delivery systems on the release of damascones more systematically. Especially by grafting them onto polymers with different backbone and side-chain structures, additional advantages such as increased precursor stability (due to the encapsulating polymer matrix), enhanced surface deposition (by specific functionalization of the polymer) or better dispersion in aqueous media (H_2O is the main solvent for all targeted applications) are expected from polymer conjugates as compared to the 'monomeric' fragrance-precursor systems described so far [6–10][12]. Previous studies on the hydrolysis of *Schiff* bases [3] or the intramolecular cyclization of 2-carbamoylbenzoates by neighboring-group participation [5][6][16] showed that the fragrance release seems to be quite sensitive to the structure of the leaving fragrance molecule and to the type of the polymer, rather than to its actual size or density at the surface.

Polymers are widely used in pharmaceutical applications (for some recent reviews, see, *e.g.*, [17]) but also increasingly in cosmetics, bodycare or household formulations, and other products that contain fragrances [1]. In particular, amphiphilic copolymers and polymer conjugates are of especial interest for the delivery of hydrophobic materials as a consequence of their formation of aggregates, which even have some mechanical stability (for some recent reviews, see, *e.g.*, [18]). Besides biocompatible poly(ethylene oxide)- or poly(ethylene glycol)-based systems, poly(acrylic or methacrylic acid) copolymers were investigated; these latter show a pH-dependent change in conformation and are strongly coiled at low pH and unfolded at higher pH [19]. In most cases, block copolymers have been studied, and much less is known about the behavior of random copolymers, which are often more easily prepared. We thus decided to investigate the release properties of damascones from amphiphilic poly(ethylene glycol), poly(methacrylic acid), and poly(vinylbenzoic acid) random copolymer conjugates, and to

compare the release properties from the polymers with those of the corresponding monomers. Besides the nature of the polymer backbone, the release properties may be influenced by the structure of the comonomer, as well as by its stoichiometric ratio with respect to the damascone-release unit.

For the present study, we chose δ-damascone (**1**) [20] as the fragrance molecule to be released by *retro*-1,4-addition from polymeric substrates. Due to their ease in preparation and their close structural relationship to the alkanoates and benzoates that have been investigated previously [12], we synthesized δ-damascone derivatives **2** and **3**, which serve as the starting point for polymethacrylate- or polystyrene-based materials, respectively. Amphiphilic copolymers **4**–**7** (*Fig. 1*) with the two different polymer backbones can be obtained by radical copolymerization (see, *e.g.*, [21]) of the hydrophobic monomers **2** or **3** with a second, hydrophilic monomer, such as **8**–**11** (*Fig. 2*). Especially in the case of comonomers **8** and **10**, the three-dimensional structure of the resulting copolymers in aqueous medium will strongly depend on the pH [19]. With the pK_a of poly(methacrylic acid) and poly(vinylbenzoic acid) homopolymers being 5.0 [22] and 7.1 [23], respectively, a strong difference in polymer conformation is expected for polymers **4** and **6** when moving from acidic to basic conditions. The pH-dependent protonation and deprotonation of copolymers **4** and **6** and the variation of the molar ratio of the different comonomers (from 1:1 to 1:5) within the polymer backbone should allow to influence both, the solubility of the copolymers in aqueous media as well as the release kinetics of the fragrance molecule. pH-Dependent structural changes are of particular interest in those types of applications where an increase of pH from acidic to neutral conditions is observed, as for example in the case of a typical fabric softener. The behavior of the polymeric delivery systems in aqueous solution is thus particularly important for the protection of the fragrance molecule during storage (at low pH) as well as for its release once deposed on the target surface (after a pH-induced structural change of the polymer at the end of the washing cycle).

2. Results and Discussion. – 2.1. *Preparation of Monomers and Polymers.* For the preparation of polymeric δ-damascone precursors, we used (±)-*trans*-3-hydroxy-1-(2,6,6-trimethyl-cyclohex-3-en-1-yl)butan-1-one (**12**) [12][20] as the starting material. Monomers **2** and **3** were then obtained in one step by reacting butanone **12** (*Scheme 2*) with methacrylic acid (=2-methylprop-2-enoic acid; **8**) or 4-vinylbenzoic acid (=4-ethenylbenzoic acid; **10**) [24], respectively, under *N*,*N*′-dicyclohexylcarbodiimide (DCC) coupling conditions [25]. Acid **10** is commercially available, or can easily be prepared in very good yields from 1-chloro- or 1-bromo-4-vinylbenzene by *Grignard* reaction with CO_2 (dry ice) [24]. Esterification of **10** with 2-[2-(2-methoxyethoxy)-ethoxy]ethanol in the presence of DCC and 4-(dimethylamino)pyridine (DMAP) gives hydrophilic monomer **11**.

Amphiphilic polymethacrylate-based random copolymers **4a**–**d** were prepared in a two-step sequence by radical polymerization [21][26] in organic solution. In the first step, monomer **2** was polymerized with 5, 3, 2, or 1 mol-equiv. of *tert*-butyl methacrylate as the comonomer by using 2,2′-azobis[isobutyronitrile] (=2,2′-azobis[2-methylpropanenitrile]; AIBN) as initiator. To separate the copolymers **13a**–**d** (*Scheme 2*) from unreacted monomers, they were precipitated several times from MeOH or heptane. Cleavage of the *tert*-butyl groups with trifluoroacetic acid in CH_2Cl_2 at room tempera-

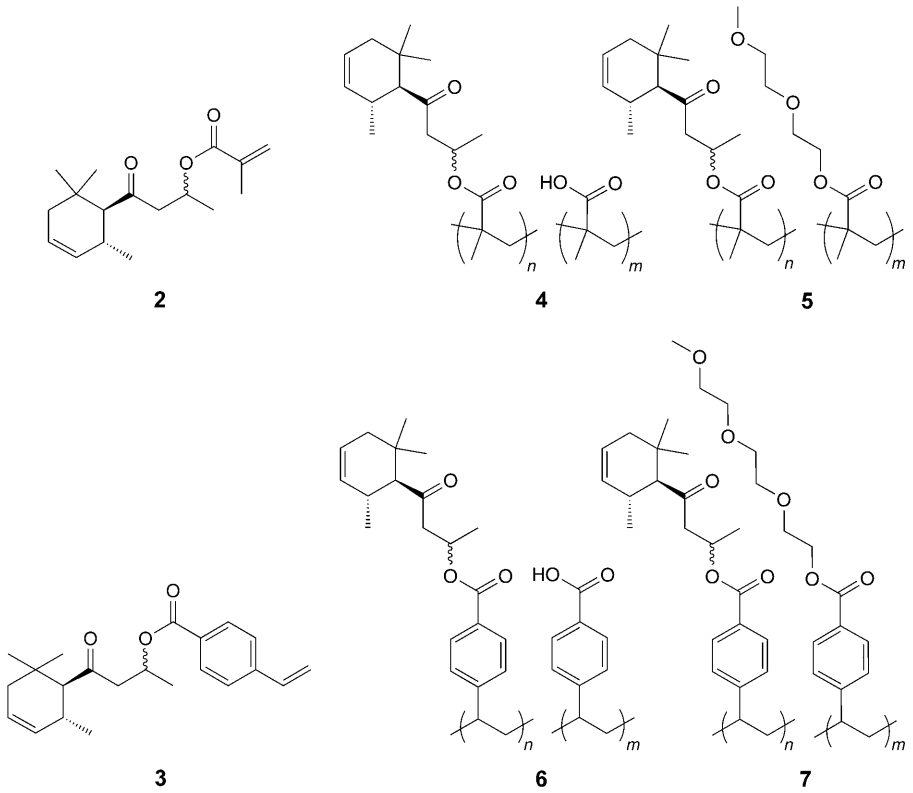


Fig. 1. *Structures of δ-damascone-containing monomers* **2** *and* **3** *together with amphiphilic polymethacrylates* **4** *and* **5** *and derived polystyrenes* **6** *and* **7**

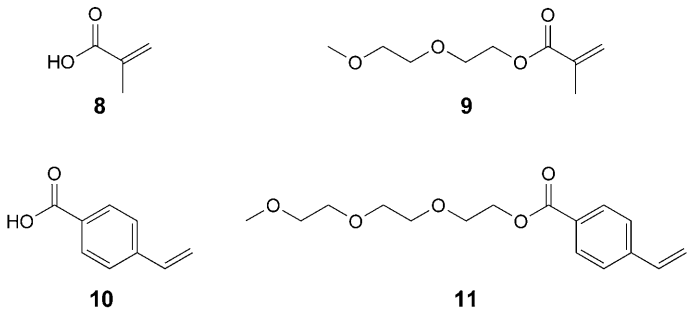
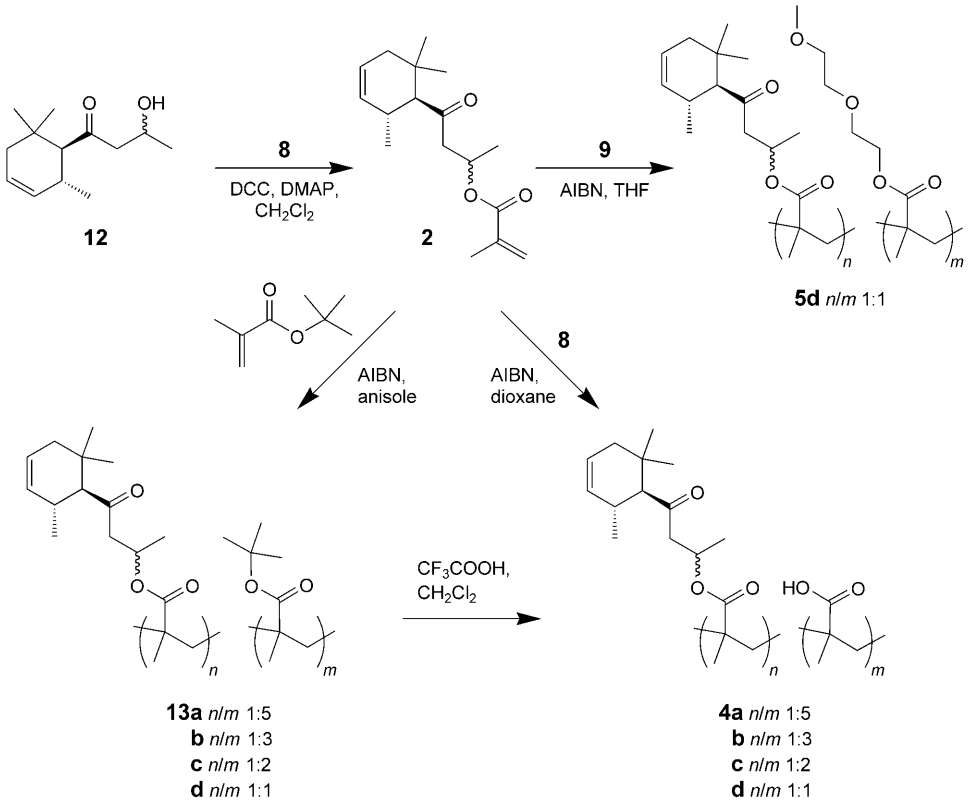


Fig. 2. *Structures of hydrophilic comonomers* **8**–**11**

ture finally led to the formation of pH-sensitive amphiphilic random copolymers **4a**–**d**, all of which were obtained as solid materials. Polymers **4a**–**d** could be prepared in one step from monomers **2** and **8** if the radical polymerization was carried out in dioxane. The two-step sequence has nevertheless the advantage that intermediates **13a**–**d** are soluble in THF and can thus be more easily characterized by analytical size-exclusion

Scheme 2. *Preparation of Polymethacrylate-Based Random Copolymers* **4**, **5**, *and* **13**



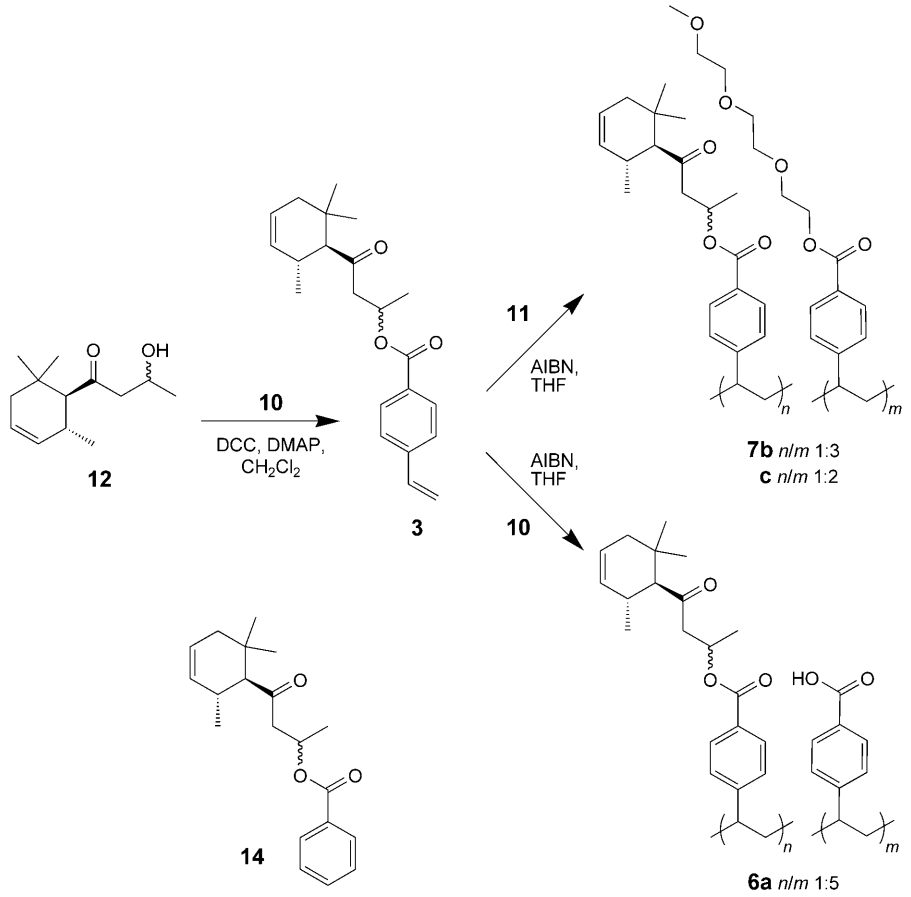
chromatography (SEC). Copolymer **5d**[1]) was obtained in one step by polymerization of a mixture of **2** and **9** in a ratio of 1:2 and in the presence of AIBN in THF.

Similarly, polystyrene derivatives **6a**[1]) and **7b**,**c**[1]), which are structurally closely related to 'monomeric' benzoate **14** [12], were synthesized by random copolymerization of **3** with styrene derivatives **10** or **11** in various proportions, respectively, in THF by using AIBN as the radical source (*Scheme 3*). Amphiphilic polymers **6a** and **7b**,**c** were obtained as solids or highly viscous oils by repetitive extraction or precipitation with heptane.

All polymers were characterized by NMR and IR spectroscopy, and their average masses were determined by SEC based on a universal calibration with commercially available poly(methyl methacrylate) (PMMA) or polystyrene (PS) standards in THF. As mentioned above, the average molecular masses of methacrylates **4a**–**c** could not be determined with the SEC method described in this work, due to their low solubility in THF. However, since the hydrolysis of the *tert*-butyl groups of **13a**–**d** does not modify the length of the polymer chains, polymers **4a**–**d** should still have the same degree of

[1]) For convenience, the key letters **a**–**d** of **4a**–**d** indicating the molar ratio of the monomers are also used for the polymers **5d**, **6a**, and **7b**,**c**.

Scheme 3. *Preparation of Polystyrene-Based Random Copolymers* **6** *and* **7**



polymerization as their corresponding analogues **13**. *Table 1* summarizes the measured average molecular masses (M_w and M_n) as well as the corresponding calculated polydispersity indices (I_p). Polymethacrylates **4a**–**d**, **5d** and **13a**–**d** were thus found to have average molecular masses between *ca.* 15000 and 60000 Da and polydispersity indices of 2.1 to 2.6. The corresponding polystyrene derivatives have much lower molecular masses varying between *ca.* 10000 and 15000 Da in the case of **7b**,**c** and 2000 Da for **6a**, with polydispersity indices between 1.3 and 1.8.

^{13}C-NMR Spectroscopy was found to be the most-convenient technique for the determination of the molecular structures of the obtained polymers, although considerable peak broadening was observed for a series of signals, and not all of the expected resonances could be clearly assigned. This is particularly true for the carboxylic acid derivatives **4a**–**d** and **6a**. Characteristic peaks at δ 211.3 (C=O), 165.4 (ester), 53.3 (CH_2), 41.7 (CH_2), or 33.1 (quaternary C) demonstrate the presence of the δ-damascone moiety in the final product. The disappearance of the *s* and *t* of the methacrylate C=C bond of monomers **2**, **8**, and **9** (at δ 136 and 125) or the *d* and *t* of the vinylben-

Table 1. *Weight-Average* (M_w) *and Number-Average* (M_n) *Molecular Masses as well as Polydispersity Indices* (I_p) *of Random Copolymers* **6a**, **7b**,**c** *and* **13a**–**d** *as Determined by Analytical SEC in THF.* Polymers **4a**–**c** were insoluble in THF. All values are rounded up to ±100.

	Standard used for universal calibration	M_w [Da]	M_n [Da]	I_p
13a	PMMA	47000	18000	2.61
b	PMMA	35800	16100	2.22
c	PMMA	54100	26100	2.07
d	PMMA	56900	24600	2.31
6a	PS	2100	1600	1.31
7b	PS	12100	7700	1.56
7c	PS	14700	8200	1.79

zoate C=C bond of monomers **3**, **10**, and **11** (at δ 136 and 116), respectively, show that remaining monomers could be removed quantitatively in all cases. Furthermore, the relation of intensities of certain resonances, such as the *q* at δ 19.9 and 59.0 in the ^{13}C-NMR spectra of polymers **5d** and **7b**,**c**, roughly reflects the expected stoichiometric relationship between the monomer containing the damascone-release unit and the copolymerized ethylene glycol derivatives.

2.2. *Evaluation of Damascone-Release Properties in the Presence of Surfactants.* As a first evaluation of our delivery systems, we compared the release of δ-damascone from monomers **2**, **3**, and **14** (*Scheme 3*) with that of amphiphilic polymers **4**–**7** under controlled conditions in acidic or alkaline buffered aqueous solution and in the presence of a nonionic or an anionic surfactant. Surfactants of different type are generally used in all types of functional-perfumery applications. Despite the fact that the surfactant is likely to influence the damascone release, its presence was expected to provide a more-realistic impression of the behavior of our delivery systems in practical applications. Furthermore, the surfactant acts as a solubilizer and thus helps to dissolve both the hydrophobic monomers and the amphiphilic polymers.

In a typical experiment, 0.25M solutions of the precursors were prepared in THF and added to different buffer solutions in H_2O/MeCN 2:1 at pH 4.97 or pH 10.48, containing 1% by weight of a nonionic surfactant (*Triton® X100*), or at pH 10.16, containing 1% by weight of an anionic surfactant (sodium dodecyl sulfate (SDS)). After stirring for 3 d, the reaction solutions were extracted with heptane, and the amount of δ-damascone released was determined by GC with external-standard calibration. To verify the loss of the damascone during the experiment and to estimate its stability in the buffer solutions, a control experiment with δ-damascone was carried out under the same reaction conditions. *Table 2* shows the results obtained for the *retro*-1,4-reaction of monomers **2**, **3**, and **14** and polymers **4**–**7** in alkaline solution in the presence of surfactants, together with the reference of unmodified δ-damascone (**1**).

The data summarized in *Table 2* indicate some interesting aspects for the behavior of the different release systems in aqueous solution containing a surfactant. The results obtained for the control sample showed that some of the δ-damascone (**1**) was lost after 3 d in the presence of the nonionic surfactant, independently of the pH and the structure of the surfactant. The loss of damascone is probably due to the undesired condensation reaction between two damascone molecules under the alkaline conditions (intermolecular 1,4-addition).

Table 2. *Comparison of the Amount* [mol-%] *of* δ-*Damascone* (**1**) *Released by* retro-*1,4-Addition from Monomers* **2**, **3**, *and* **14** *and from Amphiphilic Polymers* **4**–**7** *after 3 d at Room Temperature in Buffered Solutions of* H_2O/*MeCN 2*:*1 in the Presence of 1% by Weight of* Triton® X100 *or Sodium Dodecyl Sulfate* (SDS). All values were obtained from extraction with heptane and GC analysis with external standard calibration.

Compounds		Amount of δ-damascone (**1**) extracted in the presence of		
		Triton® X100, pH 4.97 (phosphate buffer) [mol-%]	*Triton® X100*, pH 10.48 (borate buffer) [mol-%]	SDS, pH 10.16 (borate buffer) [mol-%]
Reference:	**1**	88	83	83
Monomers:	**2**	7	76	80
	3	2	51	61
	14	8	98	71
Polymers:	**4a**	5		32
	4b	3	25	26
	4c	3	22	26
	4d	10	24	32
	5d	< 1	5	
	6a	< 1	9	17
	7b	1	15	5
	7c	0	9	

The data in *Table 2* show that both the monomeric and polymeric damascone precursors are relatively stable in acidic media but release the fragrance under alkaline conditions. The fact that the monomers release the fragrance molecule more easily than their polymeric analogs indicates that polymers seem to stabilize the release systems by slowing down the *retro*-1,4-addition as a consequence of aggregate formation, as it was originally expected during the design of the polymeric delivery systems (see above).

At pH 10, polymethacrylic acid derivatives **4a**–**d** show a constant damascone release of 20–30%, independently of the nature of the surfactant or the stoichiometric ratio between hydrophobic and hydrophilic units in the polymer backbone, whereas polystyrene derivatives **6a** and **7b**,**c** liberate less than 20% of the fragrance molecule after 3 d (*Table 2*). Furthermore, the release properties of the polystyrenes seem to be more sensitive towards the type of surfactant present (see differences observed for polymers **6a** and **7b**,**c**). The nature of the polymer backbone (polymers **4a**–**d** and **6a**), the structure of the hydrophilic comonomer (polymers **6a** and **7b**,**c**) and its stoichiometric ratio with respect to the hydrophobic damascone-release unit (polymers **7b**,**c**) are thus important parameters to be considered. As a general trend, higher amounts of δ-damascone (**1**) were released from copolymers bearing free carboxylic acid functions (**4a**–**d** and **6a**) as compared to those with the poly(ethylene glycol) side chains (**5d** and **7b**,**c**). Especially at high pH, the presence of the negative charge seems to favor the damascone-release, either as a result of a more-hydrophilic environment close to the damascone-release unit or a better dispersibility of the polymer system in aqueous media. Since the overall polymer structure is furthermore pH-dependent [19] (*vide supra*), we decided to investigate these phenomena in more detail by comparing the release of δ-damascone from polymers **4a**–**d** and **6a** in aqueous solution at different pH.

2.3. *Comparison of Damascone Release by Fluorescence Probing and Solvent Extraction at Different pH.* Pyrene is generally used as a probe to explore the hydrophobicity or hydrophilicity of aggregates in aqueous systems, since the intensity ratio of the first (at *ca.* 272 nm) and the third (at *ca.* 383 nm) vibronic bands I_1/I_3 in the fluorescence spectrum of pyrene correlates well with the polarity of its direct environment [27–29]. The value of this ratio is 1.59 when the pyrene is solubilized in H_2O (polar medium), and 0.60 in cyclohexane (apolar medium) [27]. In our case, a ratio of 1.63 was measured in a buffered aqueous solution at pH 4.0, and a value of 1.82 was obtained at pH 7.0 or 9.0. The conformation of various polymer structures has recently been studied by fluorescence probing with pyrene [19][30][31]. This technique may thus also be useful to follow conformational changes of our polymeric delivery systems at different pH, and for the investigation of the damascone release over time. In our systems, the liberation of the damascone in the *retro*-1,4-reaction generates additional free carboxylic acid functions on the polymer backbone, and thus increases the polarity of the polymer with increasing fragrance release. If this change in polarity is sufficiently pronounced, pyrene may also serve as a probe to follow the damascone release over time. In the case of quantitative damascone release, pure poly(methacrylic acid) is obtained at the end of the experiment. As a reference, we measured I_1/I_3 ratios of 1.14, 1.79, and 1.80 for poly(methacrylic acid) (2 mM) at pH 4, 7, and 9, respectively.

Since the presence of surfactants in aqueous media creates micelles which trap the hydrophobic pyrene or interact with the polymer [31], the following experiments were carried out in the absence of surfactants, to avoid the superimposition of different possible interactions. For the measurements, *ca.* 2 mM solutions of random copolymers **4a**–**d** and **6a** were dissolved in aqueous buffer solutions at pH 4.0, 7.0, and 9.0 and then mixed with a solution of pyrene to give a total pyrene concentration of $5 \cdot 10^{-7}$ M with an EtOH content of 5% in the final solution. For each copolymer, four identical solutions were prepared, which were analyzed after 0, 24, 48, and 72 h, respectively. All analyses were carried out in triplicate. For the analysis, the solutions were split into three parts. One part was used to measure the emission spectra of pyrene, which was repeated three times. Another part was extracted with heptane and analyzed by GC, the average value being obtained from three injections; the amount of δ-damascone released was determined by external-standard calibration. The remaining part of the solution served for the measurement of the particle sizes of the aggregates. To verify that none of the damascone was lost during the extraction, a control experiment with δ-damascone was performed under the same reaction conditions. The results obtained from the different measurements are summarized in *Tables 3* and *4* and illustrated in *Fig. 3*. The deviation between the corresponding intensity peak values I_1/I_3 varied less than 0.05 within the same experiment, and an average deviation of 0.08 was observed between the three measurements. The largest errors were observed at the beginning of each series (after 1–3 h), which may be due to the fact that the system had not fully reached equilibrium. In the case of the damascone extractions, an average error of *ca.* 3.5% was obtained with a maximum value around 10% (for the styrene derivatives at pH 9).

The I_1/I_3 values obtained from the fluorescence spectrum of pyrene at the beginning of the experiments reflect the hydrophilic or hydrophobic environment of the pyrene probe in proximity to the polymer backbone as a function of the pH, the nature of

Table 3. *Average* I_1/I_3 *Values of Pyrene* ($5 \cdot 10^{-7}$ M) *Measured at Constant Time Intervals at Room Temperature by Fluorescence Spectroscopy for Aqueous Solutions of Polymers* **4** *and* **6** (0.2 mM) *Buffered at pH 4, 7, and 9*. Average values of three measurements.

	Time [h]	I_1/I_3 (pH 4)	I_1/I_3 (pH 7)	I_1/I_3 (pH 9)
4a	1–3	1.17 (±0.08)	1.33 (±0.09)	1.59 (±0.09)
	24	1.21 (±0.01)	1.48 (±0.02)	1.68 (±0.01)
	48	1.21 (±0.01)	1.52 (±0.05)	1.70 (±0.04)
	72	1.21 (±0.01)	1.53 (±0.04)	1.69 (±0.02)
4b	1–3	1.16 (±0.16)	1.33 (±0.27)	1.42 (±0.24)
	24	1.20 (±0.17)	1.37 (±0.27)	1.48 (±0.23)
	48	1.27 (±0.08)	1.48 (±0.20)	1.65 (±0.08)
	72	1.27 (±0.08)	1.51 (±0.16)	1.64 (±0.02)
4c	1–3	1.14 (±0.11)	1.17 (±0.10)	1.26 (±0.10)
	24	1.17 (±0.12)	1.25 (±0.12)	1.36 (±0.12)
	48	1.22 (±0.01)	1.34 (±0.02)	1.49 (±0.05)
	72	1.24 (±0.01)	1.36 (±0.03)	1.53 (±0.07)
4d	1–3	1.19 (±0.11)	1.23 (±0.09)	1.27 (±0.09)
	24	1.25 (±0.01)	1.30 (±0.02)	1.37 (±0.01)
	48	1.25 (±0.00)	1.30 (±0.02)	1.42 (±0.02)
	72	1.26 (±0.00)	1.30 (±0.00)	1.47 (±0.05)
6a	1–3	1.19 (±0.06)	1.27 (±0.11)	1.34 (±0.09)
	24	1.18 (±0.03)	1.26 (±0.04)	1.36 (±0.01)
	48	1.17 (±0.02)	1.26 (±0.05)	1.34 (±0.06)
	72	1.17 (±0.03)	1.22 (±0.06)	1.33 (±0.05)

Table 4. *Average Amount* [mol-%] *of δ-Damascone* (**1**) *Released at Constant Time Intervals at Room Temperature from Aqueous Solutions of Polymers* **4** *and* **6** (0.2 mM) *Buffered at pH 4, 7, and 9*. All values were obtained from extraction with heptane and GC analysis with external-standard calibration; average of three measurements.

	Time [h]	δ-Damascone [mol-%]		
		(pH 4)	(pH 7)	(pH 9)
4a	1–3	1.6 (±0.7)	3.5 (±0.4)	4.1 (±0.4)
	24	2.1 (±0.7)	14.8 (±2.6)	16.3 (±5.3)
	48	2.2 (±1.0)	18.0 (±6.8)	22.4 (±8.0)
	72	2.0 (±0.5)	22.1 (±4.2)	23.8 (±6.5)
4b	1–3	0.9 (±0.5)	1.9 (±1.0)	2.4 (±1.1)
	24	1.9 (±0.8)	8.1 (±2.6)	12.3 (±3.7)
	48	2.7 (±2.0)	10.4 (±2.3)	13.9 (±2.2)
	72	2.9 (±2.2)	14.2 (±6.5)	22.4 (±9.2)
4c	1–3	1.0 (±0.4)	2.5 (±0.4)	3.6 (±0.6)
	24	1.6 (±0.5)	8.7 (±0.5)	13.8 (±3.0)
	48	1.5 (±0.5)	12.6 (±3.0)	18.2 (±1.1)
	72	1.7 (±0.6)	14.6 (±2.8)	27.4 (±9.6)
4d	1–3	1.7 (±2.1)	1.1 (±0.3)	1.9 (±1.0)
	24	1.8 (±2.2)	8.9 (±5.4)	9.7 (±0.6)
	48	1.8 (±1.6)	11.1 (±1.5)	14.8 (±3.1)
	72	1.9 (±1.8)	16.2 (±0.8)	22.7 (±8.8)
6a	1–3	1.5 (±1.2)	4.1 (±2.8)	7.8 (±4.9)
	24	2.5 (±1.4)	8.9 (±7.6)	11.3 (±7.6)
	48	3.5 (±2.2)	11.3 (±9.7)	15.1 (±10.3)
	72	2.8 (±1.8)	12.7 (±9.8)	19.3 (±12.5)

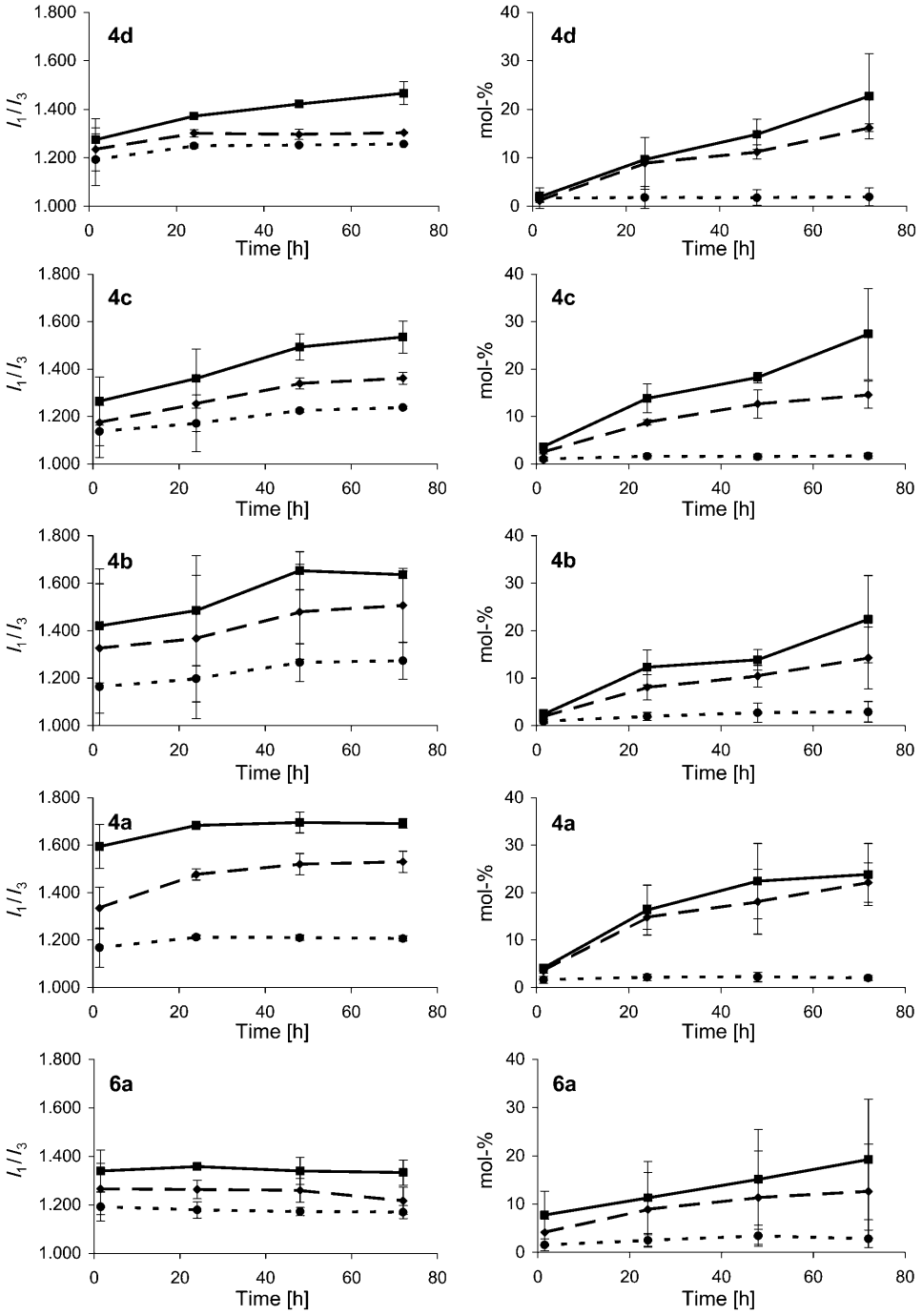


Fig. 3. *Comparison of the changes in polarity* (determined by fluorescence spectroscopy of pyrene (I_1/I_3)) *and the amount of δ-damascone* [mol-%] *released from polymers* **4** *and* **6** *at pH* 4 (···●···), 7 (-·-◆-·-), *and* 9 (—■—) *over time.* Averages of three measurements.

the polymer, and the stoichiometric ratio of the two monomers within the polymer backbone.

Concerning the influence of the pH, an increase of I_1/I_3 can be observed for all polymers when the pH varies from 4 to 9 (*Fig. 3*). This increase is quite strong for polymer **4a** (from 1.17 to 1.59) and less pronounced for polymethacrylate **4d** (from 1.19 to 1.27, *Table 3*), which is probably due to the presence of copolymer aggregates over the entire pH range and a partition of pyrene between H_2O and damascone phases. At pH 4, the values of I_1/I_3 are almost identical for all the copolymers, which is an indication of their hydrophobic character. At this pH, the copolymers form aggregates with strong H-bonding, which disperse more easily for copolymers **4b** and **4c** than for copolymer **4d**. In the case of **4b**, we measured a bimodal size distribution of *ca.* 520 nm (two peaks at 135 and 496 nm, resp.) after 1 h at pH 4, whereas polymers **4c** and **4d** were found to precipitate in H_2O. Copolymers **4b**–**d** are more H_2O-soluble at pH 7 and 9. After 3 d, polymer **4d** displays a multimodal size distribution at pH 7 and 9, with peaks centered at 16, 79, and 531 nm. At pH 9, the value of I_1/I_3 for copolymer **4a** (1.69) is very close to the value obtained when pyrene is dissolved in the aqueous buffer (1.82). This is presumably due to the high ionization of the carboxylic groups that could make the polymer shell less permeable to pyrene diffusion.

Analysis of the I_1/I_3 values of the pyrene spectrum with respect to the stoichiometric amount of carboxylic acid comonomers within the polymer chain shows almost constant values at pH 4 varying between 1.14 (**4c**) and 1.19 (**4d**). This effect is much more pronounced at high pH when the acid function is fully deprotonated. In this case, the corresponding values of I_1/I_3 increase as the amount of (protonated) carboxylic acid functions in the polymer backbone increase, and they cover a range from 1.26 (**4c**) to 1.59 (**4a**).

Furthermore, the data show that the use of pyrene as the fluorescence probe does not only allow to observe structural changes of the polymers at different pH but also to follow the release of damascone over time at constant pH. The increase of the polarity of the polymer as a consequence of the generation of additional carboxylic acid functions during the *retro*-1,4-reaction is reflected by an increase of the I_1/I_3 values of the pyrene in the case of methacrylate derivatives **4a**–**d**. This effect is more pronounced at higher pH where more damascone is released than at a lower pH where the polymer is stable. As an example, after 72 h, an increase of I_1/I_3 of 0.27 (from 1.26 to 1.53) was observed for polymer **4c** at pH 9 as compared to an increase of 0.10 (from 1.14 to 1.24) at pH 4 (*Table 3*). Extraction data revealed a release of δ-damascone of 27% in the former and 2% in the latter case (*Table 4*). In contrast to the polymethacrylates **4a**–**d**, the I_1/I_3 values of polystyrene derivative **6a** remain quite stable during damascone release at pH 4, 7, and 9.

At the beginning of the experiment, polymers **4a**–**d** form suspensions in acidic or alkaline media. With the exception of **4b**, size measurements revealed the presence of particles with a diameter above 1 μm under acidic conditions. Homogeneous dispersions are obtained the more the polymer is hydrophilic, the larger the aggregates, and the higher the pH. Polymer **4d** self-assembles at neutral pH to give particles with a diameter ranging between 2300 (after 1 h) and 756 nm (after 3 d, bimodal distribution). At a given pH, the stability increases with increasing damascone release. The same polymer is soluble in alkaline solution with an average particle size of *ca.* 16 nm (multi-

modal distribution in intensity). At pH 9, size measurements showed aggregates ranging between 560 (after 1 h) and 670 nm (after 3 d), with a constant size distribution during the experiment. This indicates a high stability of the styrene copolymer aggregates as compared to the corresponding methacrylates, and predicts a lower damascone release. Although extraction data showed that this is not the case, it should, however, be noted that solvent extraction disturbs the equilibrium by removing the damascones from the aqueous phase. It may also be possible that, in practical applications, the stronger hydrophobicity of the polymer gives rise to a stronger retention of the damascone inside the polymer, and thus slows down its evaporation (out of the polymer matrix) as compared to the corresponding methacrylates. Indeed, the direct comparison of polymer conjugates **4a** and **6a** by an expert panel in a fabric-softener application revealed that a lower intensity of δ-damascone was detected for the sample containing the polystyrene derivative. Nevertheless, this aspect needs further experimental investigation.

Interestingly, the stoichiometric ratio of damascone-release units and carboxylic acid comonomers in the polymer backbone does not seem to have a strong influence on the release of the damascone, as shown by solvent extraction. In all cases, yields between *ca.* 20 and 30% were obtained at the end of the experiment (*Table 4*). These values are within the same order of magnitude as the data obtained from the extractions carried out in the presence of surfactants (*Table 2*), with the exception of polystyrene **6a**, where about double the amount of δ-damascone was released as compared to the preceding experiment (in the presence of *Triton® X100*).

Although a quantitative correlation of the fluorescence and extraction data is not straightforward, *Fig. 3* shows that there is a reasonably qualitative fit of the curves obtained from the two techniques. The constant values obtained for the I_1/I_3 values in the pyrene spectrum in the presence of polystyrene derivative **6a** may be explained by the more hydrophobic character of the polymer as compared to the corresponding polymethacrylates **4a**–**d**. The release of the damascone has much less influence on the variation of I_1/I_3 values, which may be due to a higher retention of the released damascone in proximity of the polymer or to a preferred interaction of the pyrene with the aromatic groups of the polystyrene backbone.

3. Conclusions. – Damascones were successfully released from their polymeric β-acyloxy ketone derivatives by *retro*-1,4-addition under neutral or alkaline reaction conditions. A series of amphiphilic polymethacrylate- (see **4a**–**d** and **5d**) and polystyrene- (see **6a** and **7b**,**c**) based random copolymers were prepared by free radical polymerization of hydrophobic damascone derivatives **2** and **3** with hydrophilic comonomers **8**–**11** in various ratios by using AIBN as the radical source.

The release of δ-damascone (**1**) from various polymers was investigated in buffered aqueous solution in the presence and absence of surfactants and compared to that of the corresponding monomers by organic-solvent extraction. Whereas the monomers release damascones quite rapidly, the polymeric structures considerably slowed down the damascone release. Polymethacrylates and polystyrenes having a carboxylic acid function as hydrophilic group were found to be of particular interest for the targeted applications. In acidic media, both the monomers and the polymers were stable, and almost no damascone was released. In the case of polymethacrylates **4a**–**d** and polystyrene **6a**, an average of 20–30% of damascone release was measured after 3 d at

pH 9. The rate of damascone release can be influenced by a variety of structural parameters such as the nature of the polymer backbone, the structure and stoichiometry of the amphiphilic comonomer with respect to the damascone-release unit, and the polymer conformation in solution. Whereas the liberation of δ-damascone from polymethacrylates **4a**–**d** seems to be only pH-dependent, the release properties of the polystyrenes vary with the type of surfactant present (see differences observed for polymers **6a** and **7b**,**c**), the nature of the polymer backbone (polymers **4a**–**d** and **6a**), the structure of the hydrophilic comonomer (polymers **6a** and **7b**,**c**) and with the ratio between hydrophobic and hydrophilic repeat units in the polymer (polymers **7b**,**c**). Generally, an increasing hydrophilicity of the polymer backbone increases the amount of damascone released.

Using pyrene as a fluorescence probe permitted an investigation of the hydrophilicity or hydrophobicity of the polymer backbone as a function of the pH, and, due to the fact that the liberation of the damascone generates additional carboxylic acid functions on the polymer backbone, this technique also allowed us to follow the damascone release over time at constant pH.

As a result of the deprotonation of the carboxylic acid functions in polymers **4a**–**d** and **6a** with increasing pH, an increase of I_1/I_3 can be observed for all polymers when the pH varies from 4 to 9 (*Fig. 3*). The increase of the polarity of the polymer as a consequence of the generation of additional carboxylic acid functions during the *retro*-1,4-reaction is reflected by an increase of the I_1/I_3 values of the pyrene in the case of methacrylate derivatives **4a**–**d**. This effect is even more pronounced at higher pH where more damascone is released than at lower pH where the polymer is stable. In the case of polystyrene derivative **6a**, the I_1/I_3 value of the pyrene spectrum remains constant over time, indicating the more-hydrophobic environment of the polymer backbone, and thus better retention of the pyrene in proximity of the polymer. The fact that at pH 9 a comparable amount of δ-damascone was released from polymers **4a**–**d** and **6a** suggests that the δ-damascone may be more strongly retained inside the more-hydrophobic polymer matrix of **6a**, and thus results in a slower evaporation once deposited onto a surface. Preliminary tests in practical applications seem to confirm this hypothesis, thus suggesting that the nature of the polymer backbone has a stronger influence on the fragrance release than the ratio of hydrophilic and hydrophobic monomers within the polymer chain.

Experimental Part

General. Commercially available reagents and solvents were used without further purification if not stated otherwise. Reactions were carried out in standard glassware under N_2 or Ar, and yields were not optimized. Demineralized H_2O was obtained from a *Millipore-Synergy-185* water purifier. Column chromatography (CC): silica gel *60* (32–63 microns, from *Chemie Brunschwig*). Melting points: *Büchi-B540* melting-point instrument, at 1°/min; uncorrected. Fluorescence spectra: *Instruments-SA-Flurolog-3* spectrofluorimeter; 1-cm quartz cuvettes. Size measurements: *Malvern Zetasizer NanoSeries*; diameters in nm with diffusion at 365 nm. IR Spectra: *Perkin-Elmer-1600-FTIR* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-DPX-400* spectrometer; δ in ppm downfield from Me_4Si as internal standard, J in Hz. GC/EI-MS: *HP-5890* or *-6890* GC system equipped with a *Supelco-SPB-1* capillary column (30 m, 0.25 mm i.d.) at 70° for 10 min then to 260° (10°/min), helium flow *ca.* 1 ml/min, coupled with a *HP-MSD-5972* or *-5973* quadrupole mass spectrometer, electron energy *ca.* 70 eV; fragment ions in *m/z* (rel. int. in % of the base peak).

Analytical Size-Exclusion Chromatography (SEC). SEC Analyses were performed at r.t. (*ca.* 22°) with a system composed of a *ThermoFinnigan-Surveyor* vacuum online degasser, quaternary LC pump, autosampler, and UV/VIS detector, combined with a *ThermoSeparationProducts* (tsp) *Spectra-System-IR-150* refractometer and a *Viscotek-270-Dual-Detector* viscometer. Samples were eluted from a *Macherey-Nagel-Nucleogel-GPC-104-5* column (300×7.7 mm i.d., particle size 5 μm) at a flow rate of 1.0 ml/min by using HPLC-grade THF from *SDS* (France). Universal calibrations were carried out with the viscometer and the RI detector using commercial polystyrene (PS) or poly(methyl methacrylate) (PMMA) polymer standards from *Fluka*. *Ca.* 40 mg of the polymer standards were precisely weighed and dissolved in 10 ml of solvent, then 50 μl of these solns. were injected for the calibration.

(±)-trans-*3-Hydroxy-1-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-1-one* (**12**) can be prepared according to several methods [12][20].

4-Ethenylbenzoic Acid (**10**) [24]. A *Grignard* reagent prepared from freshly distilled 1-bromo-4-ethenylbenzene (11.00 g, 60.1 mmol), Mg turnings (1.58 g, 66.1 mmol), and a crystal of I_2 in dry THF (150 ml) was poured slowly (!) onto dry ice. The mixture was extracted with Et_2O (200 ml, 2×), washed with 10% HCl soln. (100 ml, 2×), and with a sat. NaCl soln. (100 ml, 2×). Re-extraction of the aq. phases with Et_2O, drying (Na_2SO_4), and concentration gave 8.29 g (93%) of **10**. White solid. M.p. 140–142°. ^{1}H-NMR (400 MHz, $CDCl_3$): 12.56 (br. *s* , 1 H); 8.07 (*d*, *J* = 8.2, 2 H); 7.47 (*d*, *J* = 8.7, 2 H); 6.75 (*dd*, *J* = 17.4, 10.8, 1 H); 5.88 (*d*, *J* = 17.4, 1 H); 5.39 (*d*, *J* = 11.3, 1 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 172.37 (*s*); 142.83 (*s*); 135.96 (*d*); 130.57 (*d*); 128.43 (*s*); 126.22 (*d*); 116.95 (*t*). EI-MS (commercial sample): 149 (10, $[M+1]^+$), 148 (100, M^+), 132 (9), 131 (85), 120 (3), 104 (4), 103 (34), 102 (9), 91 (3), 78 (3), 77 (22), 76 (4), 75 (4), 74 (4), 63 (3), 51 (9), 50 (5).

2-[2-(2-Methoxyethoxy)ethoxy]ethyl 4-Ethenylbenzoate (**11**). A soln. of **10** (2.00 g, 13.5 mmol), DMAP (1.30 g, 10.8 mmol), and 2-[2-(2-methoxyethoxy)ethoxy]ethanol (3.30 g, 20.3 mmol) in CH_2Cl_2 (30 ml) was cooled in an ice bath prior to the dropwise addition of a soln. of DCC (3.10 g, 14.9 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at r.t. for 2 d. The formed precipitate was filtered off and the filtrate taken up in CH_2Cl_2, and washed with 10% HCl soln. (2×), sat. Na_2CO_3 soln. (2×), and sat. NaCl soln. (2×; pH *ca.* 7). The org. layer was dried (Na_2SO_4) and evaporated. CC (SiO_2, heptane/Et_2O 1:1, then 3:7 and 1:4) and drying at 0.3 mbar for 2 h gave 3.10 g (78%) of **11**. Pale-yellow oil. R_f (heptane/Et_2O 1:4) 0.35. IR (neat): 2871*m*, 2820*m*, 1711*s*, 1650*w*, 1644*w*, 1628*w*, 1606*m*, 1566*w*, 1537*w*, 1506*w*, 1452*m*, 1402*m*, 1363*w*, 1351*m*, 1333*w*, 1310*w*, 1269*s*, 1027*m*, 1015*m*, 989*m*, 918*m*, 859*m*, 781*m*, 713*m*, 668*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.01 (*d*, *J* = 8.2, 2 H); 7.45 (*d*, *J* = 8.7, 2 H); 6.75 (*dd*, *J* = 10.8, 17.7, 1 H); 5.86 (*d*, *J* = 16.9, 1 H); 5.38 (*d*, *J* = 10.8, 1 H); 4.51–4.44 (*m*, 2 H); 3.87–3.80 (*m*, 2 H); 3.75–3.69 (*m*, 2 H); 3.69–3.61 (*m*, 4 H); 3.55–3.50 (*m*, 2 H); 3.36 (*s*, 3 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 166.27 (*s*); 141.98 (*s*); 136.02 (*d*); 130.00 (*d*); 129.25 (*s*); 126.07 (*d*); 116.49 (*t*); 71.92 (*t*); 70.72 (*t*); 70.64 (*t*); 70.59 (*t*); 69.24 (*t*); 64.11 (*t*); 59.01 (*q*). EI-MS: 262 (4), 218 (3), 176 (8), 175 (63), 174 (5), 149 (4), 148 (13), 132 (11), 131 (100), 104 (3), 103 (26), 102 (8), 101 (3), 89 (7), 88 (3), 87 (7), 77 (16), 59 (24), 58 (15), 45 (7).

*(±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate* (**2**). A described for **11**, with freshly distilled **8** (2.87 g, 33.3 mmol), DMAP (3.25 g, 26.6 mmol), **12** (7.00 g, 33.3 mmol), CH_2Cl_2 (35 ml), and DCC (7.54 g, 36.6 mmol) in CH_2Cl_2 (15 ml; addition within 20 min) for 5 d. Repetitive CC (SiO_2, heptane/Et_2O 9:1) gave 4.67 g (63%) of **2**. Pale yellow oil. R_f (heptane/Et_2O 9:1) 0.26. IR (neat): 3017*w*, 2956*m*, 2929*m*, 2872*m*, 2829*w*, 1709*s*, 1652*w*, 1636*m*, 1451*m*, 1399*m*, 1375*s*, 1352*m*, 1317*s*, 1296*s*, 1266*w*, 1250*w*, 1225*w*, 1211*w*, 1164*s*, 1136*s*, 1115*m*, 1077*m*, 1062*m*, 1030*s*, 1008*m*, 998*m*, 987*w*, 937*s*, 911*m*, 900*w*, 885*w*, 862*m*, 848*m*, 813*m*, 787*m*, 752*m*, 699*s*, 682*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.06–6.02 (*m*, 1 H); 5.58–5.49 (*m*, 2 H); 5.48–5.35 (*m*, 2 H); 3.05, 2.89 (*dd*, *J* = 17.9, 6.7, 1 H); 2.71, 2.54 (*dd*, *J* = 17.9, 6.1, 1 H); 2.58–2.46 (*m*, 1 H); 2.29–2.21 (*m*, 1 H); 2.02–1.93 (*m*, 1 H); 1.92 (*m*, 3 H); 1.75–1.66 (*m*, 1 H); 1.32 (2*d*, *J* = 6.1, 3 H); 1.02, 0.99 (2*s*, 3 H); 0.95, 0.93 (2*s*, 3 H); 0.89, 0.88 (2*d*, *J* = 7.2, 6.7, 3 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.50 (*s*); 211.20 (*s*); 166.55 (*s*); 136.63 (*s*); 136.60 (*s*); 131.80 (*d*); 131.73 (*d*); 125.15 (*t*); 125.10 (*t*); 124.19 (*d*); 124.13 (*d*); 67.03 (*d*); 66.79 (*d*); 63.04 (*d*); 62.87 (*d*); 53.21 (*t*); 41.75 (*t*); 41.71 (*t*); 33.12 (*s*); 33.09 (*s*); 31.63 (*d*); 31.53 (*d*); 29.75 (*q*); 20.69 (*q*); 19.96 (*q*); 19.93 (*q*); 19.84 (*q*); 18.34 (*q*); 18.31 (*q*). EI-MS: 193 (6), 192 (40), 177 (7), 155 (5), 149 (3), 135 (5), 124 (5), 123 (34), 122 (24), 121 (5), 109 (4), 108 (8), 107 (31), 95 (5), 93 (5), 91 (7), 87 (3), 83 (5), 82 (3), 81 (17), 79 (6), 77 (4), 70 (5), 69 (100), 67 (6), 55 (5), 53 (3), 43 (7), 42 (3), 41 (21), 39 (6).

*(±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 4-Ethenylbenzoate* (**3**). As described for **11**, with **10** (2.35 g, 15.9 mmol), DMAP (1.55 g, 12.7 mmol), **12** (4.00 g, 19.1 mmol), CH_2Cl_2 (30 ml), and DCC (3.60 g, 17.5 mmol) in CH_2Cl_2 (10 ml) for 4 d. CC (SiO_2, heptane/Et_2O 9:1) gave 4.02 g (74%) of **2**. Colorless oil. R_f (heptane/Et_2O 9:1) 0.32. UV/VIS (MeCN): 300 (sh, 830), 281 (sh, 15300), 269 (23600), 258 (sh, 16200), 213 (10900). IR (neat): 3017*w*, 2954*m*, 2929*m*, 2870*m*, 2828*w*, 1707*s*, 1651*w*, 1629*w*, 1606*m*, 1566*w*,

1507*w*, 1456*m*, 1428*w*, 1402*m*, 1375*m*, 1367*m*, 1354*m*, 1310*m*, 1270*s*, 1226*w*, 1212*w*, 1196*w*, 1177*m*, 1137*m*, 1103*s*, 1077*w*, 1062*w*, 1044*w*, 1029*m*, 1014*m*, 987*m*, 962*w*, 937*w*, 915*m*, 885*w*, 859*m*, 781*m*, 712*m*, 699*m*, 682*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.95 (*d*, *J* = 8.2, 2 H); 7.44 (*d*, *J* = 8.7, 2 H); 6.74 (*dd*, *J* = 17.7, 11.0, 1 H); 5.85 (*d*, *J* = 16.9, 1 H); 5.64–5.49 (*m*, 2 H); 5.47–5.41 (*m*, 1 H); 5.37 (*d*, *J* = 10.2, 1 H); 3.15, 2.79 (2*dd*, *J* = 17.9, 6.7, 1 H); 3.00, 2.63 (2*dd*, *J* = 17.9, 6.1, 1 H); 2.57–2.44 (*m*, 1 H); 2.27 (*t*, *J* = 10.0, 1 H); 2.03–1.93 (*m*, 1 H); 1.75–1.66 (*m*, 1 H); 1.41 (2*d*, *J* = 6.7, 6.1, 3 H); 1.04, 1.01 (2*s*, 3 H); 0.95, 0.92 (2*s*, 3 H); 0.90, 0.88 (2*d*, *J* = 7.2, 6.7, 3 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.49 (*s*); 211.25 (*s*); 165.44 (*s*); 141.81 (*s*); 136.03 (*d*); 131.79 (*d*); 131.71 (*d*); 129.83 (*d*); 129.69 (*s*); 129.65 (*s*); 126.02 (*d*); 124.20 (*d*); 124.11 (*d*); 116.38 (*t*); 67.41 (*d*); 67.17 (*d*); 63.09 (*d*); 62.90 (*d*); 53.28 (*t*); 41.73 (*t*); 41.69 (*t*); 33.14 (*s*); 33.10 (*s*); 31.61 (*d*); 31.55 (*d*); 29.76 (*q*); 20.69 (*q*); 20.11 (*q*); 20.06 (*q*); 19.87 (*q*). EI-MS: 217 (3), 193 (11), 192 (72), 177 (10), 150 (3), 149 (6), 148 (12), 137 (3), 136 (3), 135 (5), 132 (10), 131 (100), 124 (5), 123 (29), 122 (24), 121 (5), 108 (6), 107 (23), 105 (3), 103 (19), 102 (5), 95 (3), 93 (4), 91 (6), 83 (4), 82 (3), 81 (13), 79 (5), 77 (15), 70 (3), 69 (52), 67 (4), 55 (4), 43 (4), 41 (7).

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans*-2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and* tert*-Butyl 2-Methylprop-2-enoate* ca. *1:5* (**13a**). *tert*-Butyl 2-methylprop-2-enoate (0.90 g, 6.3 mmol) and **2** (0.35 g, 1.3 mmol) were dissolved in dry anisole (4 ml) prior to the addition of AIBN (12.4 mg, 0.08 mmol) under N_2. The mixture was then degassed by means of two freeze-pump-thaw cycles and heated at 90° for 6 h. The polymer was dissolved in THF and precipitated from cold MeOH (twice) to give 0.95 g (76%) of **13a**. White solid. M.p. 151–177°. IR (neat): 2975*w*, 2933*w*, 2873*w*, 2830*w*, 1717*m*, 1474*w*, 1457*w*, 1391*w*, 1366*m*, 1248*m*, 1133*s*, 1029*w*, 967*w*, 874*w*, 846*m*, 751*m*, 699*w*, 682*w*, 667*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.53 (*m*, 1 H); 5.45 (*m*, 1 H); 5.10 (*m*, 1 H); 3.06 (*m*, 1 H); 2.86 (*m*, 1 H); 2.72 (*m*, 1 H); 2.50 (*m*, 3 H); 2.36 (*m*, 1 H); 2.30–1.65 (*m*, 16 H); 1.42 (*m*, 45 H); 1.31 (*m*, 6 H); 1.20–0.74 (*m*, 25 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.32 (br. *s*); 177.47 (br. *s*); 176.66 (br. *s*); 131.73 (br. *d*); 124.28 (br. *d*); 80.91 (br. *s*); 80.82 (br. *s*); 67.84 (br. *d*); 63.05 (br. *d*); 52.89 (br. *t*); 46.23 (br. *s*); 45.34 (br. *s*); 41.72 (*t*); 33.05 (br. *s*); 31.65 (br. *d*); 29.76 (br. *q*); 27.81 (*d*); 20.73 (br. *q*); 19.89 (br. *q*); 19.62 (br. *q*); 17.82 (br. *q*); 17.63 (br. *q*). Average molecular mass (SEC, PMMA): M_w 47000 Da, M_n 18000 Da.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans*-2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and* tert*-Butyl 2-Methylprop-2-enoate* ca. *1:3* (**13b**). As described for **13a**, with *tert*-butyl 2-methylprop-2-enoate (33 ml, 2.0 mmol), **2** (0.19 g, 0.7 mmol), anisole (3.1 ml), and AIBN (4.4 mg, 0.03 mmol): 0.32 g (63%) of **13b**. White solid. M.p. 96–105°. IR (neat): 2972*m*, 2931*m*, 2876*m*, 2830*w*, 1718*s*, 1474*m*, 1458*m*, 1390*m*, 1365*s*, 1247*m*, 1133*s*, 1063*m*, 1030*m*, 998*w*, 968*w*, 941*w*, 875*w*, 846*s*, 784*w*, 750*m*, 699*m*, 682*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.53 (*m*, 1 H); 5.46 (*m*, 1 H); 5.10 (*m*, 1 H); 3.05 (*m*, 1 H); 2.86 (*m*, 1 H); 2.72 (*m*, 1 H); 2.50 (*m*, 2 H); 2.21 (*m*, 2 H); 2.12–1.63 (*m*, 8 H); 1.43 (*m*, 27 H); 1.28 (*m*, 4 H); 1.20–0.69 (*m*, 20 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.62 (br. *s*); 176.65 (br. *s*); 131.79 (br. *d*); 124.33 (br. *d*); 80.96 (br. *s*); 80.61 (br. *s*); 67.87 (br. *d*); 62.73 (br. *d*); 52.88 (br. *t*); 46.24 (br. *s*); 45.35 (br. *s*); 41.70 (*t*); 33.10 (br. *s*); 31.68 (br. *d*); 29.79 (br. *q*); 27.81 (*d*); 20.71 (br. *q*); 19.88 (br. *q*); 19.64 (br. *q*); 17.91 (br. *q*). Average molecular mass (SEC, PMMA): M_w 35800 Da, M_n 16100 Da.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans*-2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and* tert*-Butyl 2-Methylprop-2-enoate* ca. *1:2* (**13c**). As described for **13a**, with *tert*-butyl 2-methylprop-2-enoate (0.41 ml, 2.5 mmol), **2** (0.35 g, 1.3 mmol), anisole (6 ml), and AIBN (6.2 mg, 0.04 mmol): 0.36 g (52%) of **13a**. White solid. M.p. 136–149°. IR (neat): 2972*m*, 2930*m*, 2874*m*, 2828*w*, 1716*s*, 1653*w*, 1637*w*, 1456*m*, 1390*m*, 1366*s*, 1247*s*, 1133*s*, 1063*m*, 1030*m*, 998*w*, 969*w*, 939*w*, 847*s*, 751*m*, 700*m*, 682*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.53 (*m*, 1 H); 5.46 (*m*, 1 H); 5.10 (*m*, 1 H); 3.05 (*m*, 1 H); 2.84 (*m*, 1 H); 2.72 (*m*, 1 H); 2.50 (*m*, 2 H); 2.21 (*m*, 2 H); 2.12–1.63 (*m*, 6 H); 1.43 (*m*, 18 H); 1.28 (*m*, 6 H); 1.20–0.75 (*m*, 18 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.23 (br. *s*); 177.18 (br. *s*); 131.70 (br. *d*); 124.31 (br. *d*); 81.02 (br. *s*); 80.58 (br. *s*); 67.88 (br. *d*); 62.73 (br. *d*); 52.89 (br. *t*); 46.23 (br. *s*); 45.35 (br. *s*); 41.70 (*t*); 33.10 (br. *s*); 31.71 (br. *d*); 29.77 (br. *q*); 27.81 (*d*); 20.72 (br. *q*); 19.89 (br. *q*); 19.66 (br. *q*); 17.62 (br. *q*). Average molecular mass (SEC, PMMA): M_w 54100 Da, M_n 26100 Da.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans*-2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and* tert*-Butyl 2-Methylprop-2-enoate* ca. *1:1* (**13d**). As described for **13a**, with *tert*-butyl 2-methylprop-2-enoate (0.88 ml, 5.40 mmol), **2** (1.50 g, 5.4 mmol), anisole (20 ml), and AIBN (17.8 mg, 0.11 mmol): 1.60 g (71%) of **13d**. White solid. M.p. 113–131°. IR (neat): 3013*w*, 2957*m*, 2932*m*, 2876*w*, 2830*w*, 1714*s*, 1654*w*, 1601*w*, 1456*m*, 1391*m*, 1366*s*, 1248*s*, 1133*s*, 1062*w*, 1029*w*, 966*w*, 941*w*, 847*m*, 784*w*, 751*m*, 699*m*, 682*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.56 (*m*, 1 H); 5.45 (*m*, 1 H); 5.10 (*m*, 1 H); 3.06 (*m*, 1 H); 2.86 (*m*, 1 H); 2.72 (*m*, 1 H); 2.50 (*m*, 3 H); 2.21 (*m*, 2 H); 2.10–1.60 (*m*, 6 H); 1.42 (*m*, 9 H); 1.26 (*m*, 6 H); 1.20–0.80 (*m*, 12 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.29 (br. *s*); 176.98 (br. *s*); 131.69 (br. *d*); 124.30 (br. *d*); 81.05 (br. *s*);

67.91 (br. *d*); 62.72 (br. *d*); 52.89 (br. *t*); 46.10 (br. *s*); 45.36 (br. *s*); 41.70 (*t*); 33.10 (br. *s*); 31.63 (br. *d*); 29.77 (br. *q*); 27.83 (*d*); 20.76 (br. *q*); 19.89 (br. *q*); 19.62 (br. *q*). Average molecular mass (SEC, PMMA): M_w 56900 Da, M_n 24600 Da.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and 2-Methylprop-2-enoic Acid* ca. *1:5* (**4a**). Trifluoroacetic acid (15 ml) was added to a soln. of **13a** (0.90 g, 0.91 mmol) in CH_2Cl_2 (15 ml), and the mixture was stirred at r.t. for 1 h (→ orange). Precipitation into cold Et_2O then afforded 0.55 g (86%) of **4a**. White solid. M.p. 215–223° (dec.). IR (neat): 3700–2400*w* (br.), 2982*m*, 2969*m*, 2956*m*, 2935*m*, 2900*m*, 2838*m*, 1697*s*, 1474*m*, 1449*m*, 1387*m*, 1369*m*, 1252*m*, 1151*s*, 1065*m*, 1029*w*, 999*w*, 961*m*, 933*m*, 832*w*, 793*w*, 750*w*, 700*w*, 683*w*, 668*w*, 632*w*, 625*w*, 617*w*, 605*w*. ^{1}H-NMR (400 MHz, MeOD): 5.58 (*m*, 1 H); 5.49 (*m*, 1 H); 5.11 (*m*, 1 H); 3.14 (*m*, 1 H); 2.90 (*m*, 1 H); 2.67 (*m*, 1 H); 2.50 (*m*, 1 H); 2.32 (*m*, 1 H); 2.20–1.78 (*m*, 19 H); 1.75 (*m*, 2 H); 1.52 (*m*, 2 H); 1.45 (*m*, 4 H); 1.30 (*m*, 7 H); 1.11–0.73 (*m*, 32 H). ^{13}C-NMR (100.6 MHz, MeOD): 213.50 (br. *s*); 183.69 (br. *s*); 182.53 (br. *s*); 182.24 (br. *s*); 181.34 (br. *s*); 179.15 (br. *s*); 132.81 (br. *d*); 125.50 (br. *d*); 69.33 (br. *d*); 64.03 (br. *d*); 55.69 (br. *t*); 54.18 (br. *t*); 53.20 (br. *t*); 52.90 (br. *t*); 47.53 (br. *s*); 46.32 (br. *s*); 45.94 (br. *s*); 42.81 (*t*); 34.19 (br. *s*); 32.92 (br. *d*); 30.51 (br. *q*); 28.24 (br. *q*); 21.50 (br. *q*); 20.33 (br. *q*); 19.93 (br. *q*); 19.28 (br. *q*); 30.51 (br. *q*); 17.36 (br. *q*); 17.02 (br. *q*).

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and 2-Methylprop-2-enoic Acid* ca. *1:3* (**4b**). As described for **4a**, with **13b** (0.25 g, 0.4 mmol), CH_2Cl_2 (5 ml), and CF_3COOH (5 ml): 0.12 g (63%) of **4b**. White solid. M.p. 235–246° (dec.). IR (neat): 3696–2182*m*, 3205*m*, 3013*m*, 2977*m*, 2953*m*, 2932*m*, 2881*m*, 2587*m*, 1719*s*, 1694*s*, 1654*m*, 1469*m*, 1449*m*, 1385*m*, 1368*m*, 1249*m*, 1153*s*, 1030*m*, 998*w*, 932*m*, 832*m*, 789*m*, 755*m*, 700*m*, 682*m*. ^{1}H-NMR (400 MHz, MeOD): 5.58 (*m*, 1 H); 5.49 (*m*, 1 H); 5.11 (*m*, 1 H); 3.14 (*m*, 1 H); 2.90 (*m*, 1 H); 2.67 (*m*, 1 H); 2.50 (*m*, 1 H); 2.32 (*m*, 1 H); 2.20–1.78 (*m*, 10 H); 1.75 (*m*, 1 H); 1.52 (*m*, 1 H); 1.30 (*m*, 5 H); 1.11–0.73 (*m*, 18 H). ^{13}C-NMR (100.6 MHz, MeOD): 213.70 (br. *s*); 182.52 (br. *s*); 182.24 (br. *s*); 181.34 (br. *s*); 132.76 (br. *d*); 125.51 (br. *d*); 69.33 (br. *d*); 64.02 (br. *d*); 55.74 (br. *t*); 54.12 (br. *t*); 46.96 (br. *q*); 46.74 (br. *q*); 46.33 (br. *q*); 45.94 (br. *q*); 42.84 (br. *t*); 34.16 (br. *s*); 33.05 (br. *d*); 32.92 (br. *d*); 30.53 (br. *q*); 30.23 (br. *q*); 21.37 (br. *q*); 20.36 (br. *q*); 19.94 (br. *q*); 19.25 (br. *q*); 17.99 (br. *q*); 17.39 (br. *q*); 17.02 (br. *q*).

Alternatively, **4b** was prepared in one step by adding AIBN (47.4 mg, 0.29 mmol) under N_2 to a soln. of **8** (1.86 g, 21.6 mmol) and **2** (2 g, 7.2 mmol) in dioxane (38 ml). The medium was degassed by means of two freeze-pump-thaw cycles and then heated at 90° for 4 h. The polymer was precipitated from cold heptane (twice) to give 2.87 g (74%) of **4b**. White solid. Spectral data: as described above.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethycyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and 2-Methylprop-2-enoic Acid* ca. *1:2* (**4c**). As described for **4a**, with **13c** (0.30 g, 0.5 mmol), CH_2Cl_2 (5 ml), and CF_3COOH (5 ml): 0.17 g (71%) of **4c**. White solid. M.p. 223–236° (dec.). IR (neat): 3701–2324*s* (br.), 2954*s*, 2932*s*, 2872*s*, 2830*m*, 1717*s*, 1696*s*, 1452*s*, 1368*s*, 1248*s*, 1136*s*, 1065*s*, 1031*s*, 998*m*, 963*s*, 935*s*, 834*s*, 792*s*, 755*s*, 700*s*, 682*s*. ^{1}H-NMR (400 MHz, MeOD): 5.58 (*m*, 1 H); 5.49 (*m*, 1 H); 5.11 (*m*, 1 H); 3.16 (*m*, 1 H); 2.90 (*m*, 1 H); 2.66 (*m*, 1 H); 2.50 (*m*, 1 H); 2.33 (*m*, 1 H); 2.26–1.80 (*m*, 7 H); 1.74 (*m*, 1 H); 1.46 (*m*, 1 H); 1.30 (*m*, 4 H); 1.12–0.86 (*m*, 15 H). ^{13}C-NMR (100.6 MHz, MeOD): 182.20 (br. *s*); 181.27 (br. *s*); 169.39 (br. *s*); 132.76 (br. *d*); 125.51 (br. *d*); 69.28 (br. *d*); 64.03 (br. *d*); 63.89 (br. *d*); 55.68 (br. *t*); 54.08 (br. *t*); 46.72 (br. *s*); 46.31 (br. *s*); 45.92 (br. *s*); 42.83 (br. *t*); 34.17 (br. *s*); 33.08 (br. *d*); 32.91 (br. *d*); 30.53 (br. *q*); 21.49 (br. *q*); 20.56 (br. *q*); 20.40 (br. *q*); 19.97 (br. *q*).

Alternatively, **4c** was also prepared in one step as described for **4b**, with **2** (2.00 g, 7.2 mmol), **8** (1.24 g, 14.4 mmol), and dioxane (36 ml): 2.55 g (79%) of **4c**. White solid. Spectral data: as described above.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and 2-Methylprop-2-enoic Acid* ca. *1:1* (**4d**). As described for **4a**, with **13d** (0.15 g, 0.4 mmol), CH_2Cl_2 (5 ml), and CF_3COOH (5 ml): 0.10 g (77%) of **4d**. White solid. M.p. 221–226° (dec.). IR (neat): 3666–2385*m* (br.), 3013*m*, 2956*s*, 2932*s*, 2876*s*, 2830*m*, 1722*s*, 1700*s*, 1654*m*, 1459*m*, 1448*m*, 1374*s*, 1248*s*, 1135*s*, 1062*s*, 1029*s*, 936*s*, 840*m*, 789*m*, 749*m*, 700*m*, 682*m*. ^{1}H-NMR (400 MHz, MeOD): 5.60 (*m*, 1 H); 5.51 (*m*, 1 H); 5.11 (*m*, 1 H); 3.15 (*m*, 1 H); 2.90 (*m*, 1 H); 2.77 (*m*, 1 H); 2.51 (*m*, 2 H); 2.34 (*m*, 2 H); 2.26–1.63 (*m*, 8 H); 1.31 (*m*, 4 H); 1.23–0.77 (*m*, 9 H). ^{13}C-NMR (100.6 MHz, MeOD): 213.42 (br. *s*); 185.10 (br. *s*); 181.69 (br. *s*); 174.45 (br. *s*); 132.78 (br. *d*); 125.55 (br. *d*); 69.40 (br. *d*); 64.00 (br. *d*); 54.06 (br. *t*); 46.49 (br. *s*); 46.34 (br. *s*); 45.91 (br. *s*); 42.81 (br. *t*); 34.21 (br. *s*); 32.98 (br. *t*); 30.54 (br. *q*); 21.57 (br. *q*); 20.44 (br. *q*); 20.06 (br. *q*); 17.33 (br. *q*); 17.09 (br. *q*).

Alternatively, **4d** was also prepared in one step as described for **4b**, with **2** (2.00 g, 7.2 mmol), **8** (0.62 g, 7.2 mmol), and dioxane (30 ml): 1.95 g (74%) of **4d**. White solid. Spectral data: as described above.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 2-Methylprop-2-enoate and 2-(2-Methoxyethoxy)ethyl 2-Methylprop-2-enoate* ca. *1:2* (**5d**). A stirred soln. of **2** (0.15 g,

0.54 mmol) and 2-(2-methoxyethoxy)ethyl 2-methylprop-2-enoate (**9**; 0.10 g, 0.53 mmol) in dry THF (3 ml) was degassed with Ar for a few minutes. Then AIBN (3.0 mg, 0.02 mmol) was added, and the mixture was heated at 50° for 15 h. After cooling to r.t., CH_2Cl_2 (1 ml) was added and the mixture slowly poured into hexane (30 ml) to precipitate 0.23 g (94%) of **5d**. White solid. IR (neat): 3015*w*, 2954*m*, 2927*m*, 2875*m*, 2828*m*, 1721*s*, 1650*m*, 1522*w*, 1453*m*, 1373*m*, 1366*m*, 1327*w*, 1290*m*, 1247*m*, 1131*s*, 1108*s*, 1063*m*, 1028*s*, 998*m*, 984*m*, 965*m*, 940*m*, 898*w*, 860*m*, 851*m*, 806*w*, 797*w*, 787*m*, 772*w*, 748*m*, 699*m*, 682*m*, 656*w*. ^{1}H-NMR (400 MHz, (D_8)THF): 5.53 (*m*, 1 H); 5.46 (*m*, 1 H); 5.09 (*m*, 1 H); 4.07 (*m*, 2 H); 3.66 (*m*, 2 H); 3.60 (*m*, 2 H); 3.52 (*m*, 2 H); 3.33 (br. *s*, 3 H); 3.22–2.40 (*m*, 3 H); 2.28 (*m*, 1 H); 2.20–1.60 (*m*, 9 H); 1.28 (br. *s*, 3 H); 1.20–0.70 (*m*, 12 H). ^{13}C-NMR (100.6 MHz, (D_8)THF): 211.42 (*s*); 177.74 (*s*); 177.14 (*s*); 132.74 (*d*); 132.61 (*d*); 125.09 (br. *d*); 72.94 (*t*); 71.26 (*t*); 69.37 (*t*); 68.43 (br. *d*); 64.73 (*t*); 63.36 (br. *d*); 59.11 (*q*); 55.17 (br. *t*); 53.69 (*t*); 45.98 (*s*); 45.64 (*s*); 42.51 (*t*); 33.73 (*d*); 32.55 (*q*); 30.24 (*q*); 30.01 (*q*); 21.12 (*q*); 20.36 (*q*); 20.16 (*q*); 19.95 (*q*); 17.92 (br. *q*). Average molecular mass (SEC, narrow standard calibration, PMMA): *ca*. 51100 Da.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 4-Ethenylbenzoate and 4-Ethenylbenzoic Acid* ca. *1:5* (**6a**). A soln. of **3** (1.00 g, 2.9 mmol), **10** (1.30 g, 8.8 mmol, 3 equiv.), and AIBN (0.10 g, 0.6 mmol) in dry THF (20 ml) was heated under N_2 at 80° for 2 d. More AIBN (0.10 g) was added and, after another 2 d, the mixture was concentrated and the crude product redissolved in THF (3 ml) and then precipitated with heptane (4 ml, 3×). Drying at 0.3 mbar afforded 1.93 g (62%) of a white solid still containing some impurities. NMR integrations revealed an average ratio of the two monomers of *ca*. 1:5 in the final polymer **6a**. M.p. 308–318° (dec.). IR (neat): 2925*m* (br.), 2870*w*, 2644*w* (br.), 2537*w* (br.), 1685*s*, 1606*s*, 1573*m*, 1508*w*, 1448*w*, 1419*m*, 1368*m*, 1311*m*, 1271*s* (br.), 1176*s*, 1101*m*, 1046*m*, 1016*m*, 936*w*, 882*w*, 854*m*, 800*m*, 774*s*, 705*s*, 684*w*, 670*w*. ^{1}H-NMR (400 MHz, (D_8)THF): 8.10–7.40 (*m*, 12 H); 7.20–6.30 (*m*, 12 H); 5.62–5.38 (*m*, 3 H); 3.34–2.98 (*m*, 1 H); 2.98–2.62 (*m*, 1 H); 2.57–2.41 (*m*, 1 H); 2.41–2.26 (*m*, 1 H); 2.26–1.18 (*m*, 23 H); 1.18–0.68 (*m*, 9 H). ^{13}C-NMR (100.6 MHz, (D_8)THF): 211.64 (br. *s*); 167.59 (br. *s*); 165.65 (br. *s*); 150.58 (br. *s*); 132.67 (*d*); 130.58 (br. *d*); 129.81 (br. *s*); 128.39 (br. *d*); 125.06 (*d*); 124.85 (*d*); 63.28 (*d*); 54.03 (*t*); 44.46 (br. *t*); 42.50 (*t*); 41.65 (br. *d*); 33.69 (*s*); 32.56 (*d*); 30.04 (*q*); 21.08 (*q*); 20.16 (br. *q*). Average molecular mass (SEC, PS): M_w 2100 Da, M_n 1600 Da.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 4-Ethenylbenzoate and 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 4-Ethenylbenzoate* ca. *1:3* (**7b**). A soln. of **3** (0.19 g, 0.57 mmol) and **11** (0.50 g, 1.7 mmol, 3 equiv.) in dry THF (5 ml) was rapidly added to a stirred soln. of AIBN (0.05 g, 0.3 mmol) in dry THF (5 ml) under N_2. The mixture was heated at 80° for 90 h. After cooling to r.t., MeOH (1 ml) was added and the mixture concentrated. The crude product was taken up into THF (2 ml) and extracted with heptane (4–6 ml). The heptane phase was decanted and the procedure repeated twice (with 1.5 ml of THF and 3 ml of heptane). Evaporation of the heptane phases and drying at 0.3 mbar for 2 h afforded 0.39 g (56%) of **7b**. Highly viscous oil. IR (neat): 2927*m*, 2869*m*, 1711*s*, 1650*w*, 1607*m*, 1573*w*, 1507*w*, 1451*m*, 1418*m*, 1373*m*, 1366*m*, 1352*m*, 1307*m*, 1270*s*, 1197*m*, 1179*m*, 1098*s*, 1029*m*, 1016*m*, 998*w*, 985*w*, 940*m*, 853*m*, 772*m*, 707*m*, 683*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.10–7.40 (*m*, 8 H); 7.00–6.20 (*m*, 8 H); 5.61–5.39 (*m*, 3 H); 4.55–4.33 (*m*, 6 H); 3.93–3.78 (*m*, 6 H); 3.78–3.60 (*m*, 18 H); 3.59–3.47 (*m*, 6 H); 3.41–3.32 (*m*, 9 H); 3.25–2.94 (*m*, 1 H); 2.92–2.59 (*m*, 1 H); 2.58–2.44 (*m*, 1 H); 2.38–2.22 (*m*, 1 H); 2.08–1.20 (*m*, 17 H); 1.18–0.75 (*m*, 9 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 166.12 (*s*); 165.32 (*s*); 149.31 (br. *s*); 131.73 (*d*); 129.59 (br. *d*); 128.23 (br. *d*); 124.28 (*d*); 71.93 (*t*); 70.64 (*t*); 70.57 (*t*); 69.19 (*t*); 67.97 (*t*); 64.02 (*t*); 62.88 (*d*); 59.03 (*q*); 53.28 (*t*); 41.72 (*t*); 40.66 (br. *d*); 33.11 (*s*); 21.63 (*d*); 29.77 (*q*); 20.73 (*q*); 20.10 (*q*); 19.89 (*q*). Average molecular mass (SEC, PS): M_w 12100 Da, M_n 7700 Da.

*Random Copolymer of (±)-1-Methyl-3-oxo-3-(*trans-*2,6,6-trimethylcyclohex-3-en-1-yl)propyl 4-Ethenylbenzoate and 2-[2-(2-Methoxyethoxy)ethoxy]ethyl 4-Ethenylbenzoate* ca. *1:2* (**7c**). As described for **7b**, with **3** (0.29 g, 0.85 mmol) and **11** (0.50 g, 1.7 mmol, 2 equiv.): 0.53 g (67%) of **7c**. Highly viscous oil. IR (neat): 3013*w*, 2922*m*, 2870*m*, 1710*s*, 1651*w*, 1607*m*, 1573*w*, 1507*w*, 1451*m*, 1418*m*, 1374*m*, 1365*m*, 1352*m*, 1307*m*, 1270*s*, 1197*m*, 1179*m*, 1135*m*, 1098*s*, 1029*m*, 1016*m*, 999*w*, 986*w*, 940*m*, 826*w*, 852*m*, 771*m*, 707*s*, 682*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.10–7.30 (*m*, 6 H); 6.90–6.20 (*m*, 6 H); 5.61–5.39 (*m*, 3 H); 4.55–4.34 (*m*, 4 H); 3.93–3.77 (*m*, 4 H); 3.77–3.60 (*m*, 12 H); 3.59–3.47 (*m*, 4 H); 3.41–3.32 (*m*, 6 H); 3.26–2.94 (*m*, 1 H); 2.92–2.59 (*m*, 1 H); 2.57–2.44 (*m*, 1 H); 2.38–2.22 (*m*, 1 H); 2.07–1.18 (*m*, 14 H); 1.16–0.75 (*m*, 9 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 211.72 (br. *s*); 166.13 (*s*); 165.31 (*s*); 149.15 (br. *s*); 131.74 (*d*); 129.56 (br. *d*); 128.57 (br. *d*); 128.10 (br. *d*); 127.40 (br. *d*); 124.28 (*d*); 124.15 (*d*); 71.93 (*t*); 70.64 (*t*); 70.57 (*t*); 69.18 (*t*); 67.29 (br. *d*); 63.98 (*t*); 62.88 (*d*); 59.03 (*q*); 53.28 (*t*); 41.72 (*t*); 40.67 (br. *d*); 33.11 (*s*); 31.63 (*d*); 29.78 (*q*); 20.74 (*q*); 20.10 (*q*); 19.89 (*q*). Average molecular mass (SEC, PS): M_w 14700 Da, M_n 8200 Da.

Extraction Experiments in the Presence of Surfactant. Buffer solns. containing 1% by weight of surfactant were prepared by dissolving (under sonication) two buffer tablets pH 4.0 (phthalate; *Fluka*) or two buffer tab-

lets pH 9.2 (borate; *Fluka*) and 2.24 g of *Triton® X100* (*Union Carbide*) or SDS (*Sigma*) in a mixture of H_2O (160 ml) and MeCN (40 ml; 31.3 g) (4:1). To determine the exact pH of the final reaction solns., 10 ml of the buffers were diluted with 2 ml of MeCN (to give a mixture of H_2O/MeCN 2:1), and the pH was measured (*Mettler-Toledo-MP220* apparatus with an *InLab-410* Ag/AgCl glass electrode) at 20° to be 4.97 ± 0.04 and 10.48 ± 0.03 in the case of *Triton® X100*, and 10.16 ± 0.01 in the case of SDS. To 5 ml of the acidic or alkaline buffer solns. (H_2O/MeCN 4:1) were added 50 µl of a *ca.* 0.25M soln. (corresponding to the amount of damascone in the molecule) of monomers **2**, **3**, and **14**, copolymers **4**–**7**, or δ-damascone in THF, and the solns. were diluted with 1 ml of MeCN to give a final mixture H_2O/MeCN 2:1. The samples were stirred at r.t. for 3 d, then extracted with 1 ml of heptane and left decanting for 30 min. The heptane extracts (0.5 µl) were subjected in triplicate to GC (*Carlo-Erba-MFC-500* gas chromatograph; *Fisons-AS-800* autosampler; *J&W Scientific-DB1* capillary column (30 m, 0.32 mm i.d.) at 70° for 10 min then to 260° (10°/min), or at 100° to 220° (10°/min); helium pressure 50 kPa; inj. temp. 250–260°, det. temp. 240–280°). The amount of δ-damascone (**1**) was determined by external-standard calibration from five or six different concentrations in heptane, by using an average of five injections for each calibration point.

Fluorescence Probing Experiments. Fluorescence emission spectra of pyrene solubilized in copolymer solns. were recorded in the range of 360–460 nm at an excitation wavelength of 334.5 nm and pyrene concentrations sufficiently low to ensure the absence of excimers. According to the molecular mass of their repeat unit, 20–60 mg of random copolymers **4** or **6** were dispersed in 38 ml of a buffer soln. (*CertiPUR®* from *Merck*) at pH 4, 7, and 9, resp., and 2 ml of a 10^{-5} M pyrene soln. in EtOH was added. The final soln. thus contained 0.0209 mM of δ-damascone, $5 \cdot 10^{-7}$ M pyrene, and a total of 5% of EtOH. Each soln. was divided into four samples of 10 ml, three of which were pipetted into 10-ml flasks (to have no free headspace above the sample solns.). The flasks were closed and the solns. stirred at r.t. (constant at *ca.* 23°) for 24, 48, and 72 h, resp. The remaining 10 ml were analyzed immediately after preparation (after *ca.* 1–2 h). For the analysis, the samples were split, 2 ml were taken for the fluorescence measurements, 2 ml for the measurements of the particle sizes (1 ml of each soln. was analyzed in a *DTS-1060* folded capillary cell from *Malvern*), and the remaining 6 ml were extracted with 1 ml of heptane. The damascone content in the heptane phase was analyzed by GC as described above.

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