Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Designed T- and Comb-Shaped Copolymers of Poly(Ethylene Oxide) and Polyisobutylene

Alexander V. Lubnin[a]; Joseph P. Kennedy[a]
[a] The Maurice Morton Institute of Polymer Science The University of Akron, Akron, Ohio, USA

To cite this Article Lubnin, Alexander V. and Kennedy, Joseph P.(1994) 'Designed T- and Comb-Shaped Copolymers of Poly(Ethylene Oxide) and Polyisobutylene', Journal of Macromolecular Science, Part A, 31: 12, 1943 — 1953
To link to this Article: DOI: 10.1080/10601329409350109
URL: http://dx.doi.org/10.1080/10601329409350109

J.M.S.—PURE APPL. CHEM., A31(12), pp. 1943–1953 (1994)

DESIGNED T- AND COMB-SHAPED COPOLYMERS OF POLY(ETHYLENE OXIDE) AND POLYISOBUTYLENE

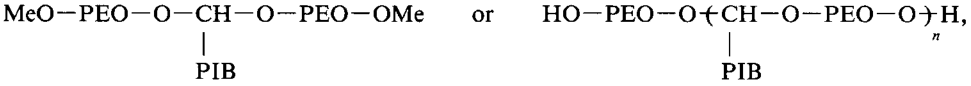
ALEXANDER V. LUBNIN† and JOSEPH P. KENNEDY*

The Maurice Morton Institute of Polymer Science
The University of Akron
Akron, Ohio 44325-3909, USA

Key Words: Polyisobutylene; Poly(ethylene oxide); Copolymers, Amphiphilic copolymers; Polyacetal; Aldehyde; Condensation; Emulsion; Hydrolytic stability

ABSTRACT

The synthesis, characterization, and select emulsification properties of T- and comb-shaped sequential copolymers comprising a poly(ethylene oxide) (PEO) backbone carrying one or multiple polyisobutylene (PIB) branches linked by acetal groups are described. Conditions have been developed under which PIBs carrying an aldehyde endgroup (PIB-CHO) react with commercially available PEOs carrying one or two hydroxyl termini (MeO-PEO-OH and HO-PEO-OH) to yield



$$\mathrm{MeO{-}PEO{-}O{-}\underset{\underset{PIB}{|}}{CH}{-}O{-}PEO{-}OMe} \quad \text{or} \quad \mathrm{HO{-}PEO{-}O{\left(}\underset{\underset{PIB}{|}}{CH}{-}O{-}PEO{-}O{\right)}_{n}H},$$

respectively. The microarchitecture and composition of these copolymers can be influenced by the CHO/OH ratio and the molecular weight of the prepolymers. These sequential copolymers form very stable oil-in-water emulsions. The linking acetal group is resistant to hydrolysis in aqueous

---

†Visiting scientist. Permanent address: S. V. Lebedev Central Synthetic Rubber Research Institute, Gapsal'skaya st., 1, St. Petersburg 198035, Russia.

suspension at room temperature, most likely because of steric protection afforded by the bulky water-repellent PIB blocks. However, the acetal linking groups can be rapidly cleaved by 1N aqueous HCl at ~100°C.

INTRODUCTION

We recently described the synthesis and characterization of linear mono- and di-aldehyde-telechelic polyisobutylenes, PIB-CHO and OCH-PIB-CHO [1]. Having on hand well-defined aldehyde-capped PIBs and commercially available MeO-PEO-OH and HO-PEO-OH, we became intrigued with the possibility of assembling various PIB/PEO sequential copolymers held together by acetal linkages. While several types of block copolymers of isobutylene (A) and ethylene oxide (B) have already been synthesized, i.e., $(AB)_n$ [2], AB and BAB [3, 4], as well as butyl rubber-*graft*-poly(ethylene oxide) [5], copolymers comprising a hydrophilic PEO backbone carrying hydrophobic PIB branches have not been described. Such amphiphilic copolymers may be of interest for a variety of uses including biomedical applications [6, 7]. This paper describes the synthesis and characterization of select PIB/PEO-based polyacetals (see formulas in Abstract), and gives some insight into the use of these materials as stable emulsifying agents.

EXPERIMENTAL

Materials

Toluene (EM Industries) was refluxed with *p*-toluenesulfonic acid (TosOH) for a week, distilled, redistilled over CaH_2, and stored over CaH_2 under nitrogen. The TosOH was obtained from its monohydrate (Fisher) by azeotropic drying with toluene and used as a 0.1 M solution in toluene. 2-Methoxyethanol (Aldrich, 99%) was dried with Drierite ($CaSO_4$) and used without further purification. Poly(ethylene oxide)s and isovaleraldehyde (97%), were from Aldrich; acetic acid, THF, molecular sieves (type 3A, beads), Drierite (8 mesh), $CaCl_2$, $NaHCO_3$, and buffer solution pH 7.4 were from Fisher and used as received.

Syntheses

The preparation and characterization of aldehyde-capped polyisobutylenes have been described [1]. The condensations of aldehydes with alcohols were carried out in glass-stoppered 250 mL round bottom flasks equipped with a Teflon-covered magnetic stirring bar under a blanket of nitrogen. The reactions were stopped by neutralizing the acid catalyst with $NaHCO_3$. Drying agent and $NaHCO_3$ were separated by centrifugation. The products were dried in vacuum at 40°C and analyzed by GPC and NMR spectroscopy.

Procedures

NMR spectra were obtained by a Varian Gemini-200 spectrometer. The conversion of aldehyde into acetal was quantitated by comparing the integrated intensity of the aldehyde proton signal ($\delta = 9.75$; $^3J_{H,H} = 2$ Hz) with that of the acetal proton ($\delta = 4.64$; $^3J_{H,H} = 5.5$ Hz). Figure 1 shows a representative spectrum together with the assignments.

GPC traces were generated by a Waters instrument. Details of both NMR and GPC techniques have been described [8].

RESULTS AND DISCUSSION

The condensation of aldehydes with alcohols to acetals is an equilibrium reaction. Therefore, to shift the equilibrium toward the product and to obtain high conversion, the water formed should be removed. This can be achieved by physical or chemical methods [9]. Chemical drying involves the addition of organic compounds (e.g., orthoesters, dialkyl sulfites) whose removal from the target amphiphilic copolymers may be difficult. Physical drying may involve azeotropic distillation of water (e.g., with toluene) or adsorption of water by solid drying agents. According to preliminary experiments, refluxing PEO in benzene in the presence of TosOH for a week leads to the formation of small but noticeable amounts of longer chains (detected by GPC). In view of this, we decided to use solid drying agents that work at relatively low temperatures and can be easily removed by centrifugation after use.

Model Reaction

To guide our synthetic efforts, a series of model reactions were carried out with isovaleraldehyde and 2-methoxyethanol which mimic the aldehyde-capped PIBs and hydroxyl-ended PEOs, respectively:

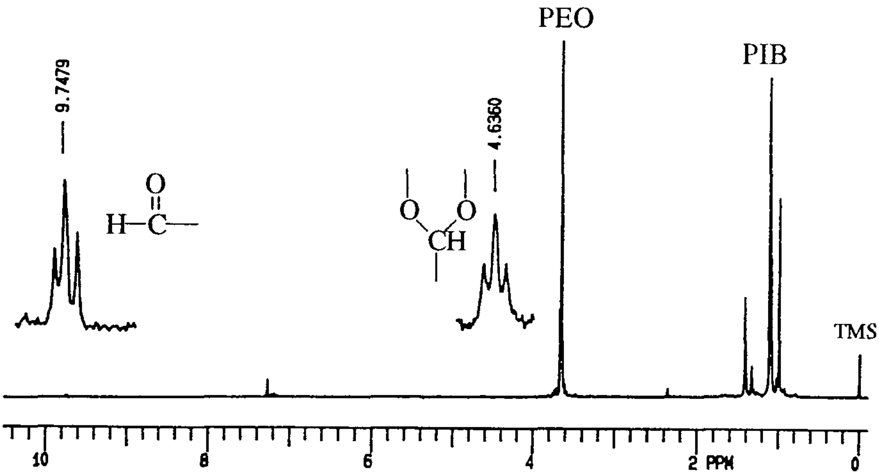


FIG. 1. ^{1}H-NMR (200 MHz) spectrum of PEO-*comb*-PIB (Exp. 3, Table 2) in $CDCl_3$. The aldehyde and acetal proton signals are enlarged and expanded.

$$(CH_3)_2CHCH_2CHO + 2HOCH_2CH_2OCH_3 \longrightarrow (CH_3)_2CHCH_2CH(OCH_2CH_2OCH_2)_2 + H_2O$$

The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. The acetal formed was isolated by vacuum distillation (bp = 107–108°C/3 mmHg) and characterized by NMR spectroscopy: ^{1}H-NMR ($CDCl_3$) $\delta = 0.92$ (d, $J = 6.6$ Hz, 6H, $2CH_3$ in *i*-Bu group); 1.55 (t, 2H, CH_2 in *i*-Bu group); 1.61–1.84 (m, 1H, CH in *i*-Bu group); 3.39 (s, 6H, $2CH_3O$); 3.52–3.79 (m, 8H, $4CH_2O$); 4.71 (t, $J = 6.0$ Hz, 1H, OCHO). ^{13}C-NMR ($CDCl_3$) $\delta = 22.9$ ($2CH_3$ in *i*-Bu group); 24.5 (CH in *i*-Bu group); 41.8 (CH_2 in *i*-Bu group); 59.2 ($2CH_3O$); 64.0, 72.3 ($4CH_2O$); 102.2 (OCHO).

A variety of solvent, drying agent, and catalyst combinations have been tested, and representative results are collected in Table 1. Apparently the condensation is more efficiently catalyzed by TosOH than by acetic acid (compare Exps. 4 and 8), and the yield is lower with $TosOH \cdot H_2O$ than with TosOH (compare Exps. 8 and 10). The process is slightly faster in toluene than in THF (compare Exps. 8 and 9). $CaCl_2$ most likely forms an insoluble complex with 2-methoxyethanol since, according to ^{1}H-NMR analysis, the latter disappears from the solution without yielding a corresponding amount of acetal, and after long stirring the system becomes an unstirrable paste. Molecular sieves were the least efficient drying agents under the conditions employed (see Exp. 7).

The data indicate the following sequences of overall activities: Catalyst: TosOH > $TosOH \cdot H_2O$ >> CH_3COOH; Drying agent: $CaSO_4$ >> $CaCl_2$ > molecular sieves 3A; Solvent: toluene > THF.

A comparison of Exps. 10 and 11 shows that the reaction may stop spontaneously. To gain insight into this phenomenon, the charge in Exp. 11 was split into two and fresh $CaSO_4$ was added to one part (Exp. 12) while 5 mmol/L TosOH was added to the other (Exp. 13). The reaction resumed only upon TosOH addition; evidently catalyst is consumed either by the formation of the $TosOH \cdot CaSO_4$ complex (which is similar to $MgSO_4 \cdot H_2SO_4$ [10]) or by esterification of the alcohol terminus: TosOH + ROH → TosOR + H_2O (similar to sulfation of alcohols [11]).

Syntheses of T- and Comb-Shaped Copolymers

Led by the information obtained in model experiments, we have studied the synthesis of T- and comb-shaped copolymers in the presence of TosOH and $CaSO_4$ in toluene solution. Scheme 1 helps to visualize the overall reactions investigated, and Table 2 shows the data.

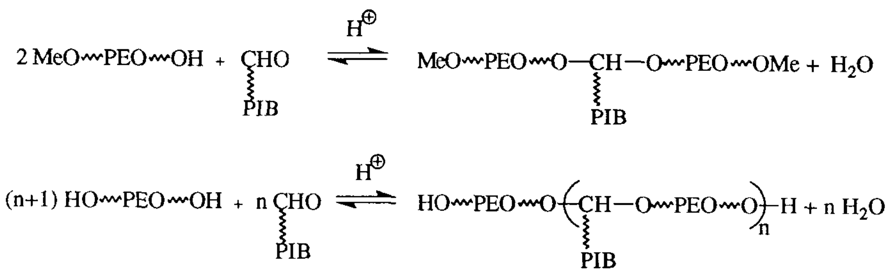
The GPC traces of the products obtained in Exps. 1 and 2 of Table 2 were virtually identical (Fig. 2a); however, upon the addition of a second aliquot of TosOH to the reaction mixture of Exp. 2, the peak corresponding to the starting prepolymers decreased by ~5% (Exp. 3, Table 2, and Fig. 2b). Evidently, just as in the case of the model reaction, the acetal formation stops but can be restarted by the addition of fresh catalyst. In line with this observation, incremental catalyst addition was employed in most subsequent experiments (see Table 2).

TABLE 1. Condensation of Isovaleraldehyde with 2-Methoxyethanol[a]

Exp.	[*i*-BuCHO]$_0$, mol/L	OH/CHO, mol/mol	Catalyst	[H$^+$], mmol/L	Drying agent	Solvent	Time	Conversion, %
1	1	5	CH_3COOH	100	Mol. Siev.[b]	Toluene	1 day	0
2	1	5	CH_3COOH	100	$CaCl_2$	Toluene	1 week	15
3	1	5	CH_3COOH	100	$CaCl_2$	Toluene	1 month	40
4	0.4	5	CH_3COOH	4	$CaSO_4$	THF	1 day	10
5	1.7	5	TosOH	7	$CaSO_4$	—	1 day	80
6	1	2	TosOH	1	$CaSO_4$	THF	2 days	70
7	0.5	4	TosOH	2.5	Mol. Siev.[b]	THF	1 day	20
8	0.5	4	TosOH	2.5	$CaSO_4$	THF	1 day	95
9	0.5	4	TosOH	2.5	$CaSO_4$	Toluene	1 day	~100
10	0.5	4	$TosOH \cdot H_2O$	5	$CaSO_4$	THF	1 day	70
11	0.5	4	$TosOH \cdot H_2O$	5	$CaSO_4$	THF	1 week	70
12	Fresh $CaSO_4$ (10 g) was added to Exp 11 after 1 day						1 + 1 day	70
13	Fresh TosOH (5 mmol/L) was added to Exp 11 after 1 day						1 + 1 day	90

[a] 50°C, drying agent: 25 g, volume = 100 mL.

[b] Molecular sieves, type 3A.



SCHEME 1. Synthesis of T- and comb-shaped copolymers of PEO and PIB.

Both GPC traces in Fig. 2 show a peak characteristic of the starting materials and three additional peaks reflecting the formation of T- and comb-shaped copolymers with $n = 1$, 2, and 3 PIB branches (see Scheme 1). The resolution of these peaks is due to narrow molecular weight distribution (MWD) of the T- and comb products obtained by the use of narrow MWD prepolymers ($\overline{M}_w/\overline{M}_n \approx 1.1$). The peak molecular weight (M_p) of the three products indicated by the numbers 1, 2, and 3 in Fig. 2 agree with the values calculated from Scheme 1: $M_p = nM_{p,PIB} + (n + 1)M_{p,PEO}$, where M_p is the GPC peak molecular weight of the products, $M_{p,PIB}$ and $M_{p,PEO}$ are those of the prepolymers, and n is the number of PIB blocks per macromolecule. The discrepancy between experimental and calculated data is less than 2%. Thus, according to GPC analysis, the reaction can be confidently described by Scheme 1.

Table 2 and Fig. 3 show the results of further representative experiments carried out to study the effect of the nature of the prepolymers and the CHO/OH ratio on the products synthesized.

The reaction between monofunctional prepolymers HO-PEO-OCH_3 and PIB-CHO (Exp. 4, Table 2) gave T-shaped product with $M_p = M_{p,PIB} + 2M_{p,PEO}$. Figure 3(a) shows the GPC trace, on the basis of which this conclusion was reached. We could not use ^{1}H-NMR quantitation in this case because the $\overline{M}_n$of the PEO used was relatively high so that the aldehyde and acetal proton signals were too weak for quantitative analysis. Thus, the conversion, (~50%, Exp. 4 of Table 2) was also calculated from the GPC trace. To this end, the signal of the refractive index detector (of the GPC) was calibrated with a series of prepolymer blends.

In Exp. 5 (Table 2), the molar ratio HO-PEO-OH/PIB-CHO was 1.5. The product was a mixture of relatively short macromolecules with a small number of PIB branches ($n = 1, 2, 3$) (Fig. 3b). However, when the HO-PEO-OH/PIB-CHO ratio was unity (Exp. 6, Table 2), higher molecular weight products with more PIB branches ($n = 1$-4, etc.) were obtained (Fig. 3c). Such a dependence of the length of polymers formed on the ratio of reagents is characteristic of condensation polymerizations and can be used to control the degree of polymerization.

An attempt was made to synthesize an H-shaped copolymer (four PEO blocks connected by one PIB link) by using 1 mole of OCH-PIB-CHO plus 4 moles of HO-PEO-OCH_3 (Exp. 7, Table 2). However, the conversion was relatively low (~40% estimated by GPC analysis) and the expected product was formed only in minute amounts.

TABLE 2. Conditions for PEO-PIB Copolymer Syntheses[a]

Exp.	PIB	$\overline{M}_n$, g/mol	PEO	$\overline{M}_n$, g/mol	$[CHO]_0$, mol/L	OH/CHO	$[H^+]$, mmol/L	Time, days	Conversion of aldehyde into acetal, %
1	PIB-CHO	900	HO-PEO-OH	600	0.45	2.7	20	1	—
2	PIB-CHO	900	HO-PEO-OH	600	0.45	2.7	20	2	—
3	Fresh TosOH was added to Exp. 2						20 + 20	2 + 2	70[b]
4	PIB-CHO	600	HO-PEO-OCH_3	2000	0.07	4	40 + 20	2 + 2	50[c]
5	PIB-CHO	600	HO-PEO-OH	600	0.47	3	30 + 30	1 + 2	70[b]
6	PIB-CHO	600	HO-PEO-OH	600	0.24	2	15	2	60[c]
7	OCH-PIB-CHO	2900	HO-PEO-OCH_3	2000	0.06	4	45 + 45	2 + 2	~40[c]

[a] 60°C; typically the total volume was 25 mL and 5 g Drierite was added.

[b] Determined by ^{1}H-NMR spectroscopy.

[c] Calculated from GPC data.

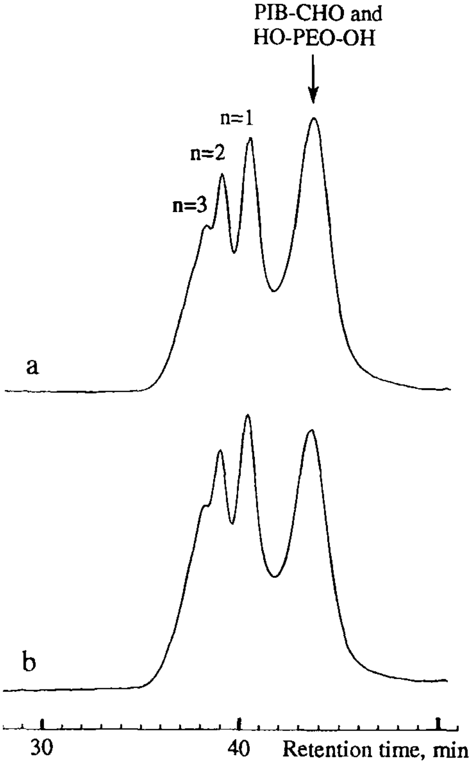


FIG. 2. GPC traces of PEO-PIBs: (a) Exp. 1 (and 2); (b) Exp. 3 (Table 2). The numbers indicate the number of PIB branches per macromolecule (*n* in Scheme 1).

According to the representative examples in Table 2, the overall composition and microarchitecture of the sought T- and comb copolymers can, to a certain extent, be controlled by varying the functionality of the prepolymers, their molecular weights, and the OH/CHO ratio. However, due to the incomplete conversion of the aldehyde, the products are always contaminated with the starting prepolymers.

Emulsification Experiments

In view of the highly amphiphilic nature of our T- and comb-shaped copolymers, it was of interest to examine their emulsification behavior with water.

First, we ascertained that neither a mechanical blend of equal amounts of HO-PEO-OH and PIB-CHO nor the model acetal $(CH_3)_2CHCH_2CH(OCH_2CH_2OCH_3)_2$ form emulsions in water. In contrast, stable aqueous emulsions were readily formed with various products of Table 2. Thus, shaking various quantities of the products whose synthesis is outlined in Table 2 with water gave opaque milky emulsions which remained stable for at least 3 months. Similarly stable emulsions

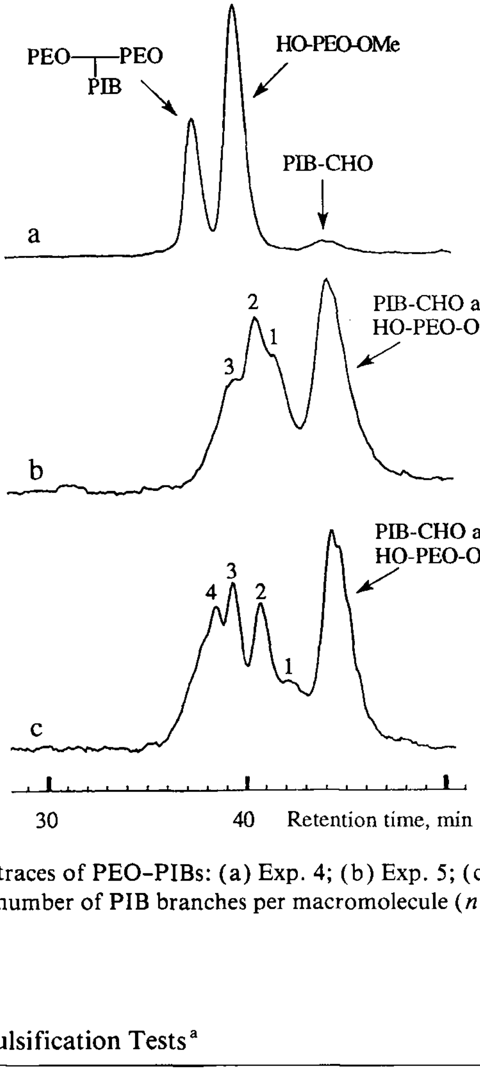


FIG. 3. GPC traces of PEO-PIBs: (a) Exp. 4; (b) Exp. 5; (c) Exp. 6 (Table 2). The numbers indicate the number of PIB branches per macromolecule (*n* in Scheme 1).

TABLE 3. Emulsification Tests[a]

	Emulsified volume, %		
Polymer[b] in toluene, wt%	Toluene/H_2O 2/18, mL/mL	Toluene/H_2O 5/15, mL/mL	Toluene/PBS[c] 5/15, mL/mL
0.12	10	35	[d]
1.25	100	[d]	30
5	100	100	50

[a] Polymer solutions in toluene were shaken with water (20 mL total volume) and stored at room temperature. Emulsified volume, upper milky layer, was measured after 3 days.

[b] Product from Exp. 3, Table 2.

[c] Aqueous phosphate buffer, 0.05 M, pH 7.4.

[d] No clear separation between emulsified and aqueous phases.

were also formed when we attempted to purify crude products by precipitation from toluene into methanol.

To estimate the emulsifying efficiency of PEO-PIB copolymers, emulsions were prepared by briefly shaking water with toluene solutions containing various quantities of the product obtained in Exp. 3, Table 2 (20 mL total volume). The mixtures were stored at room temperature for 3 days, and the volume of the emulsified layer was determined. This procedure is similar to that used by Japanese authors [5]. Table 3 shows the data. The results obtained indicate that a small amount of polymer can efficiently turn the water/toluene systems into uniform stable emulsions.

Hydrolytic Stability of PEO-PIB Copolymers

Acetals are frequently used as protective groups for aldehydes because they are less reactive and can be readily hydrolyzed back to aldehydes [12]. In view of this, we have examined the hydrolytic stability of our acetal-linked copolymers. We theorized that the relatively large hydrophobic PIB moiety in the proximity of the acetal linkage might keep water out of reach of the acetal group and thus retard or even prevent hydrolysis. To verify this hypothesis, the hydrolytic stability of copolymers was compared with that of the model acetal $(CH_3)_2CHCH_2CH(OCH_2CH_2OCH_3)_2$. Thus we prepared 1 wt% aqueous emulsions of neat polymers formed in Exps. 5 and 7 (Table 2) and visually inspected their appearance while storing them at room temperature. The stability of the emulsion is a sensitive indicator for the hydrolytic stability of the acetal groups since the cleavage of the latter should lead to the loss of the amphiphilic nature of the polymers and result in coagulation. After 5 months the milky appearance of these emulsions did not change, indicating that under these conditions the acetal groups linking the PEO and PIB segments were hydrolytically stable. In contrast, the low molecular weight model acetal, when shaken with 5 volumes of water, was completely hydrolyzed within 1 week at room temperature. The hydrolysis was followed by quantitative ^{1}H-NMR spectroscopy, i.e., by monitoring the appearance of the aldehyde proton signal ($\delta = 9.75$) and disappearance of the acetal proton signal ($\delta = 4.71$) as a function of time. Evidently, the bulky PIB segment protects the hydrolytically sensitive acetal groups from cleavage.

The hydrolytic stabilities of the model acetal $(CH_3)_2CHCH_2CH(OCH_2CH_2OCH_3)_2$ and copolymers were also compared under forcing conditions, i.e., in acidic medium. The model compound was extremely unstable: 1 mL of the model acetal was completely hydrolyzed within 5 minutes of shaking with 5 mL of 1 N HCl at room temperature. The organic layer isolated after 5 minutes was pure isovaleraldehyde without any traces of parent acetal which is also water insoluble. In contrast, under the same conditions, 1% emulsion prepared in 1 N HCl with the product from Exp. 3 (Table 2) was stable for a week. After 10 days of storage at room temperature, the first signs of a second lower clear layer became noticeable. These observations are also in line with the steric stabilization of acetal linkage by hydrophobic PIB block.

Heating the emulsion in 1 N HCl to reflux breaks the emulsion within minutes and leads to coagulation.

According to these experiments, the hydrophobic PIB block efficiently protects the adjacent acetal linkages against hydrolysis at room temperature. However, the emulsifying activity of these nonionic detergents can be controlled since rapid hydrolysis can be effected at ~100°C.

CONCLUSIONS

Novel T- and comb-shaped sequential copolymers comprising a poly(ethylene oxide) backbone carrying one or multiple poyisobutylene branches linked by acetal groups have been synthesized. These amphiphilic copolymers form stable oil-in-water emulsions. In contrast to low molecular weight model acetal, the linking acetal group in copolymers is resistant to hydrolysis in aqueous suspension at room temperature. This is most likely due to steric protection afforded by the bulky water-repellent PIB blocks. However, the acetal linking groups can be rapidly cleaved by hot aqueous HCl. Thus the emulsifying ability of these polymers can be controlled.

ACKNOWLEDGMENT

This article is based upon work supported by the National Science Foundation under Grant DMR-89-20826.

REFERENCES

[1] A. V. Lubnin, J. P. Kennedy, and B. L. Goodall, *Polym. Bull., 30,* 19 (1993).
[2] R. H. Wondraczek and J. P. Kennedy, *Ibid., 4,* 445 (1981).
[3] J. P. Kennedy and Y. Hongu, *Ibid., 13,* 115 (1985).
[4] J. P. Kennedy, *Polym. J., 17,* 29 (1985).
[5] S. Yamashita, K. Kodama, Y. Ikeda, and S. Kohjiya, *J. Polym. Sci., Polym. Chem. Ed., 31,* 2437 (1993).
[6] M. S. Munro, A. J. Quattrone, S. R. Ellsworth, P. Kulkarni, and R. C. Eberhart, *Trans., Am. Soc. Artif. Intern. Organs, 27,* 499 (1981).
[7] M. S. Munro, R. C. Eberhart, N. J. Maki, B. E. Brink, and W. J. Fry, *Am. Soc. Artif. Intern. Org. J., 6,* 65 (1983).
[8] A. V. Lubnin and J. P. Kennedy, *Polym. Bull., 29,* 9 (1992).
[9] F. A. J. Meskens, *Synthesis*, p. 501 (1981).
[10] R. D. Goodenough and V. A. Stenger, in *Comprehensive Inorganic Chemistry*, Vol. 1 (J. C. Bailar Jr., H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Eds.), Pergamon Press, Oxford, 1973, p. 657.
[11] S. R. Sandler and W. Karo, *Organic Functional Group Preparations*, Vol. 3, Academic Press, New York, 1972, p. 116.
[12] T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd ed., Wiley, 1991, p. 175.

Received January 14, 1994
Revision received March 8, 1994