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(27) In an experiment of type (a) (at constant $T = T_K$ temperature) $\eta \simeq (c - c_K(T_K))^\beta$ $c > c_K$ is in fact the critical concentration of demixing at a lower temperature T_K': $c = c_K(T_K')$. c_K being a derivable function of T_K, we get $\eta \simeq (\mathrm{d}c_K/\mathrm{d}T)^\beta (T_K' - T_K)^\beta \simeq (\mathrm{d}c_K/\mathrm{d}T)^\beta (\Delta T/T_K)^\beta$.
(28) See ref 11, Chapter 10.
(29) It is in fact assumed that the thermodynamical potentials may be split into a singular part whose first derivatives are all zero and a regular part (such as eq 12 for the free energy) which yields the critical line (eq 20). The singular part is only responsible for the (nonclassical) critical divergencies near the critical line. Such an assumption is usually made in the study of ternary systems. See, for example: Leung, S. S.; Griffiths, R. G. *Phys. Rev. A* **1973**, *8*, 2670.
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(35) The values found for $2\nu_t$ in ref 12 range from 1.18 to 1.50 (theory predicts 1.26) and the value for d that one can extract from ref 12 is $d \simeq 1.26$. It seems that, because of the low molecular weight of the chains ($M_w < 10^5$), the asymptotic règime is not reached for the system (PS/PDMS) of ref 12. For example c_K does not scale like $M^{-0.62}$, except for the two longer chains.
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(42) Strictly speaking the proportionality factor in eq 42 may depend very weakly on molecular weight (cf. eq 53). We neglect this dependence which does not change the qualitative conclusion of this section.

On the Cooccurrence of Demixing and Thermoreversible Gelation of Polymer Solutions. 1. Experimental Observations

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ABSTRACT: The phase diagram of the system 2-propanol/poly(n-butyl methacrylate) (2-POH/PBMA) was determined for two narrowly distributed polymer samples of M_w ca. 500 000. Demixing curves were measured viscometrically and visually and gelation curves by means of the velocity of a falling body. A third curve (situated within the two-phase region and also resulting from viscosity measurements), which can be related to the aggregation of droplets of the segregated phase upon cooling, is also presented. The evaluation of the gelation conditions for homogeneous solutions according to Eldridge and Ferry yields 37 kJ/mol of cross-links for the heat of gelation. Measurements with lower molecular weight PBMA (M_w 8900) confirm the cooccurrence of phase separation and gelation, although the stability of the gels against shear is rather low in this case. The exchange of the Θ-solvent 2-POH against ethanol, 1-propanol, 1-butanol, or n-decane does not reveal principal differences.

Introduction

Thermoreversible gelation has been described for biological systems[1-3] and a variety of synthetic polymers in solutions, such as PVC,[4,5] polystyrene,[6-11] and polyethylene.[12,13] In many cases gelation occurs together with phase separation[3,6,14,15] where the two phenomena have been suggested to be closely associated. For example, in concentrated aqueous solutions of barium poly(styrenesulfonate), gel points and cloud points nearly coincide.[16] The exact gelation mechanism is in most cases still a matter of controversy.

Gelation of long side-chain poly(alkyl acrylates) has been reported[17-21] to be closely related to their structure. In this series of papers the thermoreversible gelation of solutions of a relatively short side-chain poly(*n*-alkyl methacrylate), namely poly(*n*-butyl methacrylate) (PBMA), and factors influencing the network formation are studied. In the first paper, gelation and phase separation of PBMA solutions are investigated by viscometry and cloud point measurements. In the second part, a study of the thermodynamic characteristics of the system 2-propanol/PBMA and ethanol/PBMA will be reported, and in the last paper of this series, a total view concerning the experimental observations and possible molecular interpretations will be presented.

Experimental Section

Materials. Anionically polymerized samples of poly(*n*-butyl methacrylate) (PBMA) were kindly furnished by Röhm GmbH (Darmstadt, West Germany). The following materials were investigated: PBMA 2050 (0.23), PBMA 520 (0.17), PBMA 470 (0.11), and PBMA 8.9 (0.12). The numbers after the abbreviation of the polymer give the weight-average molecular weights in $\times 10^{-3}$, and those added in parenthesis give the molecular nonuniformity $U = (M_w/M_n) - 1$. All products were obtained by fractionation of the original materials from solutions in acetone; normally methanol was used as the precipitant, except for PBMA 8.9, where 10 vol % water had to be added. The fractionation was necessary to remove the high molecular weight tail of the distributions. According to ^{13}C NMR and analysis of the α-methyl groups, the high molecular weight samples contain about 60% syndiotactic and 4% isotactic triades.

The solvents ethanol (EtOH) and 2-propanol (2-POH) were analytical grade, purchased from Merck (Darmstadt, West Germany). *n*-Decane was purum and bought from Fluka (Buchs, Switzerland). All liquids were thoroughly dried over molecular sieves and used without further purification.

Procedures. Viscosity measurements were carried out in two different viscometers, supplied by Haake Messtechnik (Karlsruhe, West Germany) in order to check whether phase separation and gelation temperatures can be determined from flow behavior.

The viscometer RV 100/CV 100 allows normal rotational measurements and oscillatory ones with amplitudes between 1 and 39°. With the concentric cylinder system 15 of Haake, which is of the Mooney–Ewart type, viscosities between 1 and 10^6 mPa s can be measured. By means of the apparatus RV 2 and the cup-and-bell shaped measuring system (NV) in combination with the measuring heads MK 50 and MK 500, rotational measurements are possible up to ca. 10^4 mPa s. For the investigation of phase-separated systems, the use of a measuring system of the cone-and-plate type (PK: cone angle, 0.3°; diameter, 14 mm) turned out to be superior.

All instruments were tested and calibrated by means of Newtonian oils supplied by Haake (Eichöle 200 and 2000).

Cloud point measurements were performed visually. The solutions were considered to be phase separated as soon as a mark on the back side of a tube became invisible; the accuracy of this procedure is normally of the order of ±0.05 K.

Gelation measurements were carried out with homogeneous gels, which were made by sealing the appropriate amounts of polymer and solvent in a glass tube containing a magnetic stir bar. The tubes were placed in an oven at 60 °C and periodically inverted until homogeneous products were obtained. The magnetic stir bar was then moved to the top of the solution, placed in a vertical position, and held there by another magnet on the outside of the tube. After that, each solution was quenched in a thermostat to 5–10 °C below its gel temperature and allowed to gel for 2 h; longer gelation times to 24 h did not reveal any differences in the subsequent measurements. After gelation, the external magnet was removed because the gel was now capable of supporting the magnet.

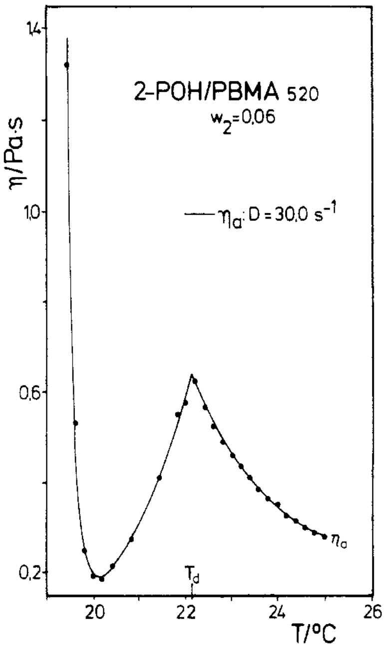

Figure 1. Temperature dependence of the apparent viscosity η_a for the system 2-propanol/poly(*n*-butyl methacrylate) M_w = 520 000 at the indicated weight fraction w_2 of the polymer and shear rate D; T_d denotes the visually determined demixing temperature.

For the quantitative determination of the gelation temperature, the temperature in the thermostat was increased in steps of 1–2 °C and the system allowed to equilibrate for ca. 30 min, after which the sedimentation velocity of the magnet was measured. This procedure was repeated in order to obtain the variation of the sedimentation velocity v with temperature for each concentration. To determine the gel temperature, a straight line was drawn through the points just above T_{gel}, and the intersection of this line wih the temperature axis was taken as the gel–sol transition. With this method the gel temperatures were reproducible within 0.5 K. It was ascertained that the shape or external surface of the falling body does not change the results outside the above range of reproducibility.

Results and Discussion

Most measurements were performed with solutions of PBMA 520 and PBMA 470 (i.e., the intermediate molecular weights) in 2-propanol. In the region of the lower polymer concentrations, only rotatory viscosity measurements could be done to test the feasibility of determining demixing temperatures T_d and gelation temperatures T_{gel} (Figure 1). For the solutions of higher concentrations with sufficiently large viscosities, additional oscillatory measurements were made on the viscometer CV 100/RV 100 at different frequencies of oscillation. Some results are shown in Figure 2, where the complex viscosity η^* is depicted as a function of temperature in addition to the apparent viscosity η_a, obtained from rotatory measurements. From these data the phase separation temperatures can clearly be seen by the peaks in $\eta^*(T)$, whereas the reascent at still lower temperatures only indicates that gelation has become predominant but does not give the true gelation temperature.

The dependence of the complex viscosity on temperature for different frequencies of oscillation is shown in Figure 3. It is interesting to note that the thickening upon cooling, i.e., the development of physical cross-links, is almost totally suppressed at the higher rates of oscillation.

Gelation and phase separation of solutions of the lowest molecular weight PBMA 8.9 in 2-propanol and in ethanol were also studied viscometrically in the cup-and-bell (NV) and in the cone-and-plate (PK) measuring systems. Ac-

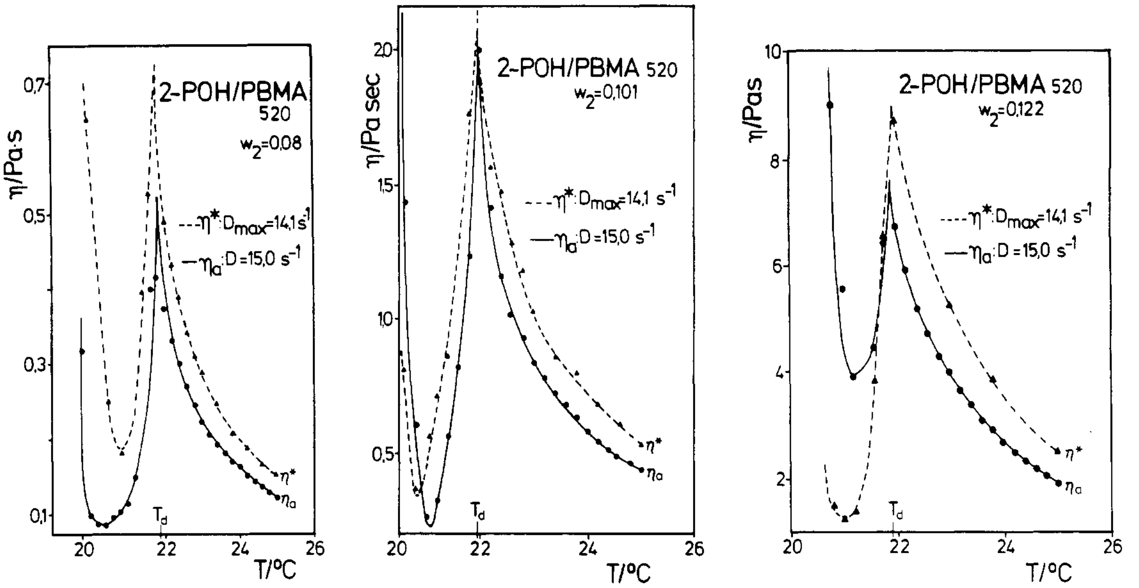

Figure 2. Temperature dependence of the apparent viscosity η_a and of the complex viscosity η^* for the system 2-POH/PBMA 520 and the indicated weight fractions w_2 of the polymer and shear rates D.

cording to observation with the naked eye, these solutions also gel, despite the extremely low molecular weight of the polymer, if its concentration is high enough.

For 2-POH and the NV system, the viscosity increases until the occurrence of phase separation, which is—as normal—associated with a steep decrease. The geometry of this measuring system seems to be unsuited for the investigation of gelation taking place after demixing, because the polymer-rich phase concentrates at the bottom of the rotor recipient at low shear rates and is therefore removed from the measuring gap so that a reascent due to gelation cannot be observed, despite the very low shear rates. This situation is seen from Figure 4 for a weight fraction w_2 of polymer equal to 0.45; that diagram also contains the results obtained with the PK system for the same solution. Under these conditions the entrance into the two-phase region is no longer detectable and the viscosity increase can be followed well down to temperatures where the system at rest has already gelled, according to observation with the naked eye.

Figure 5 shows the results with EtOH instead of 2-POH and a comparably high concentration of PBMA 8.9; in this case it is possible with the NV, as well as the PK device, to monitor the entrance into the two-phase region. No reascent indicating the visually observable gelation can, however, be seen, probably due to the higher shear rates, which already disrupt the physical cross-links. The conclusion can therefore be drawn that the mechanical stability of the physical network leading to gelation is particularly low in the case of the low molecular weight PBMA.

To check whether different Θ-solvents behave differently, the gelation of the high molecular weight PBMA 2050 was visually studied for solutions of 10 wt % in ethanol, 1-propanol, 2-propanol, and 1-butanol. All systems gel similarly at comparable polymer concentrations and distances from the precipitation thresholds, showing pronounced syneresis, where the rate of segregation of the solvent decreases in the order EtOH > 1-POH > 2-POH > BOH. After 2 days, however, all four systems had formed two distinct phases. Furthermore, it was checked whether phase separation is also accompanied by gelation, if hydrocarbons are used as Θ-solvents instead of alcohols; the results with the system *n*-decane/PBMA 520 revealed that the two phenomena cooccur as with the alcohol solutions studied in greater detail.

All experimental data concerning the phase separation and gelation of the solutions of PBMA 520 and 470 (stemming from two different fractionation processes of the same anionically prepared product) in 2-POH are summarized in Figure 6. Reduced scales have been chosen to eliminate the slight displacement of the curves belonging to the two different fractions (cf. legend of Figure 6). It can be seen from this graph that the gel curve intersects the cloud point curve at approximately the 3.5-fold thermodynamical critical concentration (which according to unpublished data corresponds to a ca. 7-fold coil-overlap concentration) and extends well into the two-phase region, becoming sigmoidal in shape at low concentrations. This behavior is similar to that of aqueous PVA solutions[14] and solutions of PS in nitropropane.[7]

The concentration of the solutions determines whether the system gels at a temperature within or outside of the two-phase region. The highly concentrated solutions produce clear gels at temperatures above the two-phase region. When cooled below their corresponding cloud point temperatures the gels become turbid. On the other hand, solutions of low concentration produce only turbid gels at temperatures well below their corresponding cloud point temperatures. When such a system is quickly quenched below T_g, turbid "homogeneous" stable gels are formed which only show a small degree of microsyneresis but no complete macroscopic separation. When it is cooled down slowly, however, two distinct phases are formed, where only the more concentrated yields a turbid gel.

Figure 6 shows another, viscometrically obtained curve which lies inside the miscibility gap. It represents the conditions of minimum viscosity (shown in Figures 1–3) and is subsequently called an inversion curve for the following reason: Starting from phase separation conditions and reducing the temperature initially results in a reduction of the viscosity, because of the transference of increasing amounts of polymer from the continuous to the suspended phase. Upon further cooling, however, the viscosity rises again because of the interactions leading to gelation; under the prevailing conditions they manifest themselves in the aggregation of the droplets of the suspended phase. The inversion curve gives the locus, at which the above two effects on the temperature dependence of the viscosity exactly balance. It should be noted,

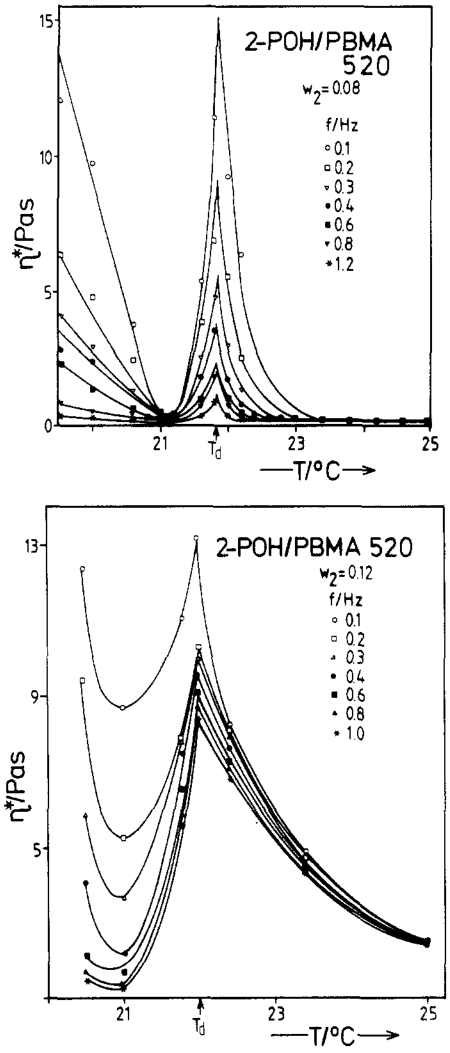

Figure 3. Temperature dependence of the complex viscosity (measured in the RV 100/CV 100 system with an oscillation amplitude of 10°) for solutions of poly(n-butyl methacrylate) (M_w = 520 000) in 2-propanol, containing 8 (a) and 12 wt % of the polymer (b), respectively. The frequencies of oscillation are given in the graph; the corresponding maximum shear rates ranged from 1.6 to 18.8 s^{-1}. T_d denotes the visually determined demixing temperature.

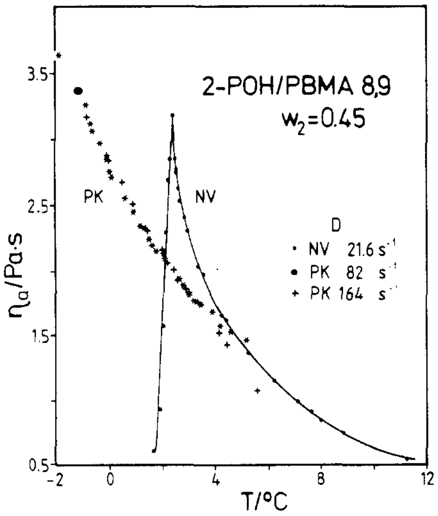

Figure 4. Temperature dependence of the apparent viscosity of a solution of poly(n-butyl methacrylate) (M_w = 8900) in 2-propanol containing 45 wt % of the polymer; the measuring systems and the corresponding shear rates are given in the graph (NV, cup-and-bell shaped; PK, cone-and-plate).

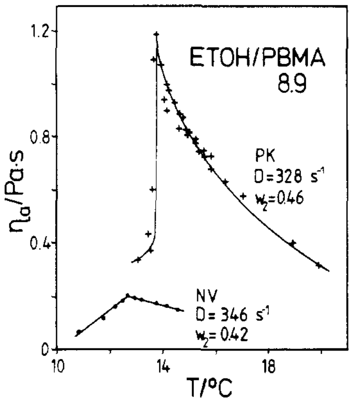

Figure 5. Temperature dependence of the apparent viscosity of solutions of poly(n-butyl methacrylate) (M_w = 8900) in ethanol, containing 42 and 46 wt % of the polymer, respectively. The measuring systems and the corresponding shear rates are given in the graph (NV, cup-and-bell shaped; PK, cone-and-plate).

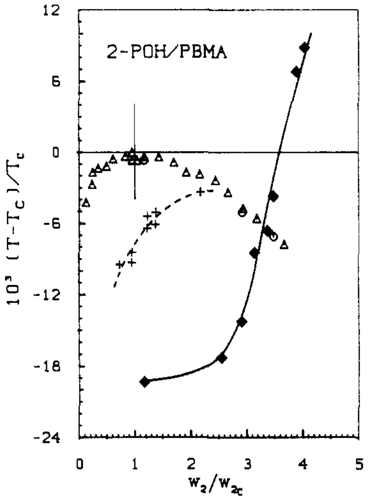

Figure 6. Phase diagram of the system 2-propanol/poly(n-butyl methacrylate) reduced to the thermodynamic critical conditions taken to be identical with the maxima of the cloud point curves for the present polymer fractions PBMA 520 (critical temperature T_c = 22.3 °C and critical weight fraction of polymer w_{2c} = 0.082) and PBMA 470 (T_c = 21.6 °C, w_{2c} = 0.086). The gelation curve (—) stems from sedimentation measurements; the inversion curve (···) (cf. text) is based on direct viscometric information.

however, that these inversion points and in particular the reascent of the viscosity obviously strongly depend on shear rate, since it governs the breaking down of the agglomerates; hence this curve should not be mistaken as a true gelation curve.

As mentioned in the Experimental Section, gelation temperatures were determined by extrapolating the velocity $v(T)$ of a falling body to zero. Since the corresponding dependences showed a distinct upward curvature in particular at higher temperatures, it seemed interesting to check whether this behavior (corresponding to a more than exponential increase in viscosity on a reduction of T) can be described by the WLF equation.[22,23] Figure 7 shows the corresponding evaluation in which log v is plotted as a function of $x/(51.6 + x)$, where $x = T - T_{gel}$. This graph demonstrates that the experimental data can indeed be linearized on the basis of the WLF equation, irrespective of polymer concentration for gelation within the homogeneous region; for the gel formation inside the solubility gap, a parallel shift of the straight lines toward higher log v values is observed. Concerning the nature of the gels it should further be noted that their examination under a properly thermostated polarized microscope showed no

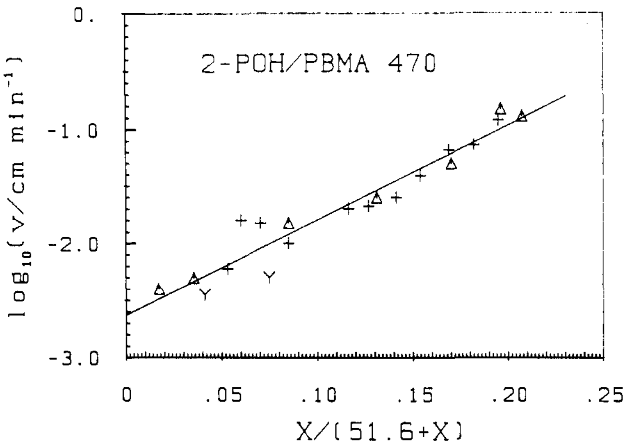

Figure 7. Plot of the sedimentation velocities v of a falling body according to the WLF equation;[22,23] $x = T - T_{\text{gel}}$, where T_{gel} was determined as described in the text. The weight fractions of the polymer are as follows: (Δ) 0.30, (y) 0.33, and (+) 0.35.

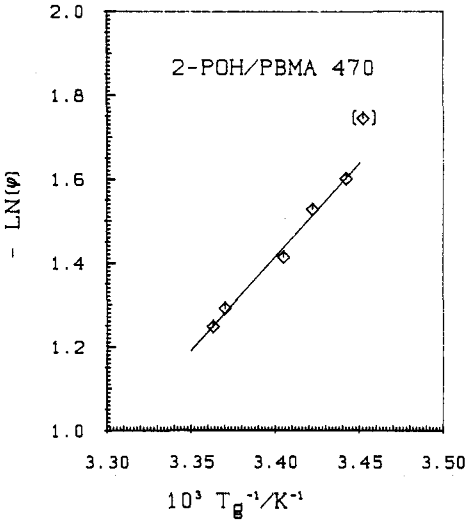

Figure 8. Evaluation of the gelation temperatures measured for the system 2-propanol/poly(n-butyl methacrylate) (M_w = 470 000) according to eq 1; φ is the volume fraction of the polymer.

indication of anisotropy whatsoever.

The data of Figure 6 for the gelling of the solutions can be fitted to eq 1 of Eldridge and Ferry,[1] who treated reversible gelation as an equilibrium between actual and potential network junction sites

$$\ln \varphi = C + \frac{\Delta H_x}{RT_{\text{gel}}} \qquad (1)$$

The plot of $\ln \varphi$ vs. $1/T_{\text{gel}}$ is represented in Figure 8. From the slope of the straight line, a value of −37 kJ/mol is calculated for ΔH_x. According to Harrison et al.[24,25] this energy (which is on the same order as that obtained for other gelling systems) corresponds to the addition of 1 mol of potential network junction points to the already formed network junctions.

The comparison of ΔH_x with other thermodynamic quantities allows one to estimate the number of monomers taking part in the formation of a network junction, as will be shown in the third paper of this series.

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Registry No. PBMA, 9003-63-8; $H_3CCH(OH)CH_3$, 67-63-0; H_3CCH_2OH, 64-17-5; $H_3C(CH_2)_2OH$, 71-23-8; $H_3C(CH_2)_3OH$, 71-36-3; $H_3C(CH_2)_8CH_3$, 124-18-5.

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