

# Chapter 11

## Rheology Control Agents for Cosmetics

Isamu Kaneda

**Abstract** “Usage feeling” is one of the most important characteristics of cosmetics, particularly skin-care products. Because the usage feeling of cosmetics is strongly related to their rheological properties, the ingredients, which affect the rheological properties of the product, are key factors in the development of skin-care products. In this chapter, two types of novel rheology control agents for cosmetics that have been developed are described. The first is hydrophobically ethoxylated urethane, which contains a relatively large C24 hydrophobe. This telechelic polymer forms a transient network structure in aqueous systems. Because the transient network structure is due to physical interactions, it is easily destroyed and reconstructed. This interesting physical property creates a unique usage feeling for use in skin-care products. The second agent is a water-swallowable microgel that was polymerized in a W/O microemulsion system. Although water-soluble polymers are widely used in cosmetics as viscosity thickeners, the thickeners often suffer a serious problem, so-called spinability, which is due to the entanglement of polymer chains. In contrast, microgels avoid such problems. The details of these rheology control agents, their syntheses, physicochemical properties, and rheological properties are reviewed.

**Keywords** Cosmetics • Rheology control agent • Telechelic polymers • Microgels

### 11.1 Introduction

For cosmetic development, a very important challenge is the control of rheological properties. Because cosmetic products, especially skin-care products, are used every day and continuously, usage feeling, which includes “spreadability,” “freshness,” and “moistness,” is an important evaluation criterion used by consumers to select a product. Therefore, the usage feeling of cosmetic products must be considered from the first stages of formulation. Undoubtedly, the usage feeling is strongly related to the rheological properties of the ingredients. Therefore, rheological

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measurements and analyses are indispensable tools for cosmetic formulators and scientists. Cosmetic products contain many kinds of ingredients, and the cosmetic formulators must make the best choice to formulate a product that is preferred by consumers.

Most skin-care cosmetics are O/W emulsions. The oil phase of the emulsion is comprised of emollient ingredients that act on the stratum corneum of the skin. In the aqueous phase, polyols such as glycerin have been used as a moisturizing ingredient. A high inner-oil phase emulsion has “body” without any viscosity thickeners [30]. For example, a semisolid O/W cream, using swollen lamellar gels, is widely utilized in skin-care products [33]. There is little demand for rheology control agents for these semisolid emulsions; however, they are needed for the formulation of emulsions that contain less inner-oil phase.

Because most skin-care products are O/W emulsions, rheology control agents are added to the continuous phase, that is, the aqueous phase. Consequently, most are water-soluble or water-swellaible polymers. Undoubtedly, nowadays, the most popular rheology control agents for cosmetics are cross-linked polyacrylic acids and their analogues [10, 38]. Cross-linked polyacrylic acid is considered a microgel. Carbopol, a well-known cross-linked polyacrylic acid, forms a porous structure in the aqueous phase. This structure results in a good “body” feeling, and the product exhibits shear-thinning, non-Newtonian flow [24, 31]. This behavior is preferred in rheology control agents for cosmetic products.

Polysaccharides are also used in cosmetics, and those used are known to be safe and nontoxic. For example, xanthan gum, which is an extracellular polysaccharide secreted by the bacterium *Xanthomonas campestris*, is widely utilized not only in cosmetics but also in foods, in personal care products, and in other fields. In particular, because this polysaccharide has a rigid structure, the formation of a porous 3D structure, which occurs at a certain critical concentration, gives “body” to the product.

“Shear-thinning, non-Newtonian flow” is a key term in the consideration of the rheological properties of cosmetic products [7, 27]. In the next section, we review the current demands in rheological properties for cosmetic products.

## 11.2 Importance of Rheology Control for Cosmetic Products

### 11.2.1 Usage Feeling and Rheology Control

There are two characteristic factors that determine the usage feeling of cosmetics. These are the “primary feeling” and the “secondary feeling” [6]. Yielding characteristic and shear thinning are strongly related to “primary feeling,” which is the usage feeling during the removal and application of the cosmetic formulation. These formulations require “body” when they are taken out of the bottle; otherwise they drip or run down the skin. Subsequently, the applied formulation is spread

and rubbed on the skin. The most important usage feeling in this situation is spreadability. Therefore, products exhibiting shear-thinning, non-Newtonian flow are preferable because of their good spreadability.

Rheological properties, such as shear-thinning flow accompanied by yield stress, are not only important for reasons of consumer palatability but, also, from a psychological view point. The psychological effect of such non-Newtonian flow behavior creates the feeling of cosmetic penetration. Generally, because the skin surface is hydrophobic, the aqueous phase of the cosmetic does not penetrate the skin immediately. The emollient effect of skin-care cosmetic products is due to moisture retention in the outer part of the skin surface. However, consumers often desire that cosmetic products applied to the skin penetrate the skin. A shear-thinning, non-Newtonian fluid with finite yield stress may satisfy these consumers because changes in viscosity create the sensation of product penetration.

In addition to “primary feeling,” both the “secondary” and “after feelings” are important. “Secondary feeling” is the usage sensation felt when rubbing the cosmetic product on the skin. Because cosmetic products are spread in a thin film on the skin, the “secondary feeling” relates to tribological properties between the skin and the hands or fingers. The feeling after application of the cosmetic product is called the “after feeling.” A sticky “after feeling” is unacceptable for consumers. This unpleasant feeling is strongly affected by the polymers added as a rheology control agents; therefore, careful consideration of rheology control agent is necessary.

### ***11.2.2 The Properties of the Polymer Solutions***

Here, we review the fundamental properties of polymer solutions to aid understanding of the following sections. Although polymer chains are isolated in dilute solutions, over their critical concentration, the chains are in contact. This is the so-called overlap concentration,  $c^*$ . The value of  $c^*$  depends on the type of polymer and its molecular weight. Generally, high molecular weight polymers and rigid polymers have small  $c^*$  values.

Polymer solutions that have concentrations in excess of  $c^*$  are called “semi-dilute solutions” or “concentrated solutions.” In such solutions, entanglement of the polymer chains occurs. Because the entanglement points act like cross-link points in gels, the solutions are viscoelastic. However, entanglement is temporary; consequently, the elastic properties disappear after a finite time length. The lifetime of the temporary cross-links is estimated by determining the relaxation time of the transient network structure using a rheological measurement method.

The temporary viscoelastic properties of cosmetic emulsions containing polymers in a semi-dilute regime affect the tribological characteristics, that is, those concerning the “secondary feeling.” Too much entanglement causes “spinability,” an undesirable usage feeling. The “after feeling” is also affected by the polymers. The nonvolatile ingredients of cosmetic products remain on the skin after

evaporation of water. Consequently, polymers in the cosmetic products condense on the skin. It is easy to imagine that the polymer entanglement increases during this process and the firmly entangled polymer chains can cause an unpleasant sticky feeling on the skin. Therefore, if too high a concentration of polymer is used in the cosmetic, various problems concerning the usage feeling can arise.

As mentioned above, the polymer concentration should be minimized to avoid unfavorable usage feelings. Moving forward, we will show practical issues for the use of polymers in cosmetic products, in particular, skin-care cosmetic products.

### ***11.2.3 Practical Issues for the Application of Polymers as a Rheology Control Agent***

#### **11.2.3.1 Acid and Salt Resistance**

Because the addition of a small amount of polymer is beneficial, polyelectrolytes that have large radii of gyration or intrinsic viscosities are preferred, for example, polyelectrolytes that have groups that can dissociate such as carboxylic acid groups. Because these dissociated groups are more polarized, in aqueous solutions, the polymers are hydrated and dissolve in water. Moreover, the dissociated groups act as fixed points of charge on the polymer chains, and the repulsive interactions between these charged groups cause expansion of the polymer chains. This effect causes high viscosity, thickening the emulsion. Cross-linked polyacrylic acid, one of the most popular rheology control agents, contains carboxyl groups. The solubility of the polyacrylic acids is low in acidic media and the turbidity is high; that is, their aqueous solution never become completely transparent. In contrast, in alkaline solutions, the polymers dissolve well, and the resultant aqueous solutions are transparent. The appearance of products, such as lotions, that contain almost no oil is important. Therefore, if a polyacrylic acid is used in such a product, the alkalinity of the formulation must be carefully controlled.

When the active ingredient is a salt, increasing the concentration of the salt increases the ionic strength. The increasing counterion concentration shields electrostatic repulsion around the dissociating groups, even at a suitable pH, and the viscosity reduces. Consequently, the polymer concentration must be increased to obtain the desired viscosity. However, as mentioned previously, increasing the polymer concentration can lead to unfavorable effects, such as an unpleasant “after feeling.”

#### **11.2.3.2 Realization of Drastic Shear Thinning**

Shear thinning is a common non-Newtonian flow behavior that occurs in many materials, including polymer solutions, emulsions, liquid crystals, and suspensions [5]. As mentioned in Sect. 11.2.1, it is desirable that shear thinning is drastic;

that is, the difference between the viscosity at the low shear rate and high shear rate is large. The ultimate goal of increasing the viscosity at low shear rates is to produce a finite yield stress. For example, percolated microgels may exhibit yield stress and shear-thinning, non-Newtonian flow properties if there are sufficient soft particles [9, 41]. Carbopols, a class of polyacrylic acid, are rheology control agents that enable this drastic shear thinning, but they have poor acid resistance. However, microgels polymerized with a monomer containing a strong acid, such as sulfonic acid, may overcome this disadvantage.

Polymers applied in sufficient concentrations exhibit shear-thinning, non-Newtonian flow due to entanglement. However, polymers in cosmetic emulsions may remain on the skin after application and subsequent evaporation of moisture. Remaining polymer condenses and becomes more firmly entangled. Such firmly entangled polymer chains can cause a “sticky feeling” on the skin. In the development of cosmetic formulations, the “after feeling” must be considered. The degree of the polymer chain entanglements depends on the length of the polymer chains; therefore, the use of relatively short polymer chains may avoid such a problem. However, short polymers do not cause sufficient viscosity thickening. To avoid this contradictory situation, temporary 3D network structures can be used. Hydrogels consisting of temporary 3D network structures, made by physical interactions such as hydrophobic interactions, are promising materials. Because the network structures are fragile, the hydrogels flow easily under shear deformation, yet they have “body” when not stressed.

Two practical examples of these novel rheology control agents developed using concepts mentioned are described in the following sections. One example is a hydrogel that consists of telechelic polymers. In this hydrogel, temporary 3D network structures are formed in the hydrogel. The second example is a water-swelling microgel, which is polymerized in a confined space leading a spherical particle shape.

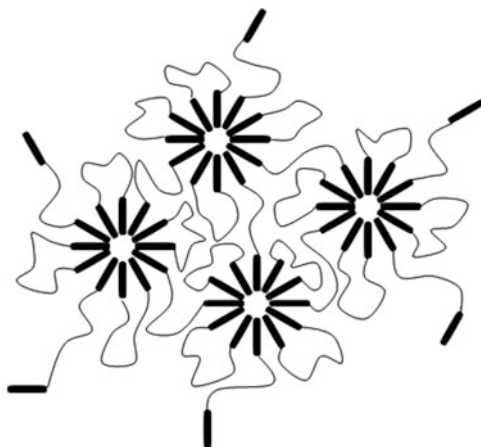
## 11.3 C24HEUR as a Rheology Control Agent for Cosmetics

### 11.3.1 *Telechelic Polymer*

Telechelic polymers are a class of associating polymers. The polymers are linear chains containing reactive end groups. When the polymers dissolve in water, the hydrophobes form self-assembled structures. Because the assemblies act as a temporary cross-linker, the solution forms hydrogels. A conceptual illustration of the 3D-network structure for the temporary hydrogels is shown in Fig. 11.1.

As shown in Fig. 11.1, hydrophobic alkanes form self-assemblies called “flower micelles.” The flower micelles are connected together by “elastic active chains” and some polymers exist as “dangling chains.” The flower micelles work as cross-link points in hydrogels comprised of telechelic polymers. Because the molecular

**Fig. 11.1** Conceptual illustration of the self-assemblies of associating telechelic polymers



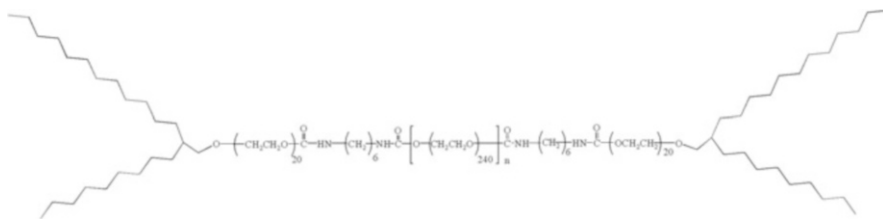
assemblies form via hydrophobic interactions, the binding energy is lower than that of covalent bonds. Therefore, cross-links are easily broken under deformation or stress. Therefore, aqueous solutions of telechelic polymers are shear thickening at low shear rates and shear thinning at higher shear rates [28, 29].

Hydrophobically modified ethoxylated urethanes (HEURs) are typical examples of these raw materials that are currently used. The first industrial application of HEURs was as rheology control agents in water-based paints [11], which contain polymer latex. Paint formulations containing HEURs cause fewer spatters when rolled onto surfaces; in addition, they show good leveling characteristics. Consequently, HEURs are promising rheology control agents for formulations that require shear-thinning, non-Newtonian flow on yield stress, for example, cosmetics. Because the required flow performance is dependent on the product, the flow properties of the material must be adjusted by changing its chemical structure. The flow properties of HEURs strongly depend on the size of the water-soluble chains and hydrophobic end chains [3, 8, 42]. Because it is easy to chemically modify HEURs, they can be easily adapted for different applications.

### ***11.3.2 The Fundamental Characteristics of C24HEUR***

Yoshida et al. [42] developed a HEUR for use in cosmetic formulations. The end-cap groups contain C24 alkanes; therefore, the polymer is named C24HEUR. The chemical structure of C24HEUR is shown in Fig. 11.2.

The fundamental characteristics of C24HEUR have been investigated. The most important characteristic is the critical concentration for formation of “flower micelles.” The dependence of polymer concentration on hydrodynamic size was investigated by dynamic light scattering (DLS). The CONTIN routine was used to analyze the time correlation function. The hydrodynamic radius was calculated



**Fig. 11.2** The chemical structure of C24HEUR

using the Stokes-Einstein equation, Eq. 11.1:

$$R_h = \frac{k_B T}{6\pi\eta D} \quad (11.1)$$

$k_B$  is the Boltzmann constant,  $T$  the absolute temperature,  $\eta$  the viscosity of the solvent (water), and  $D$  the mutual diffusion coefficients determined by DLS. Figure 11.3 shows the size distribution of the associated structure at various concentrations.

A monomodal peak appeared at 0.1%, indicating that micelles comprised of C24HEUR are present at that concentration. The  $R_h$  at this concentration is approximately  $10^2$  nm. Although this value is larger than the expected size of micelles comprising C24 alkenes, the hydrodynamic size of the micelles is larger due to the presence of “loop chains.” When the polymer concentration increases,  $R_h$  also increases. In particular, large associated structures appear at concentrations greater than 0.7%, as shown schematically in Fig. 11.1. This indicates that a connected porous structure forms above this critical concentration.

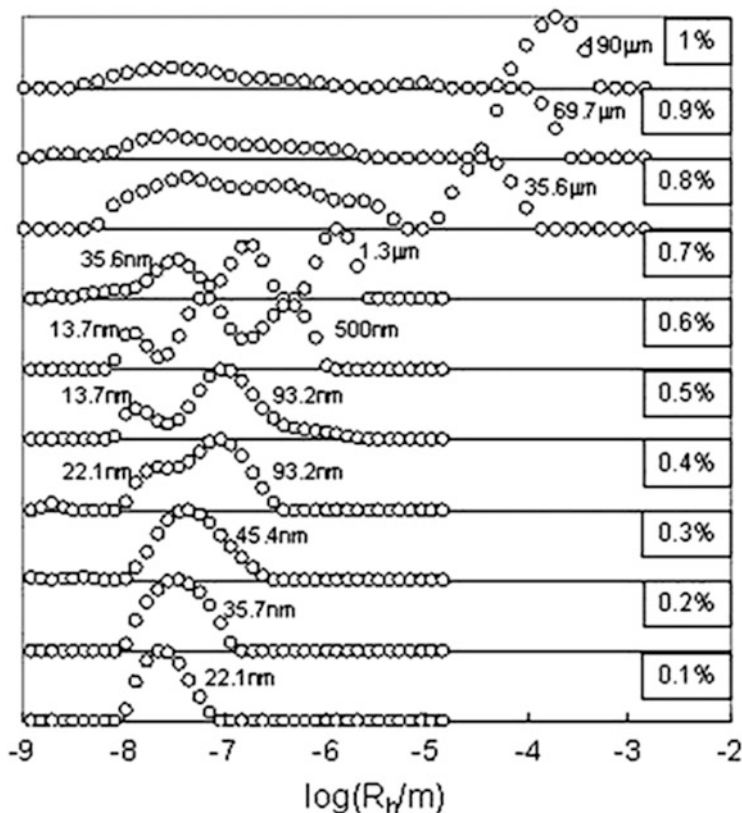
The most distinguishing rheological properties of HEURs in aqueous solution are their linear viscoelastic properties [2]. It is well known that the dynamic modulus is well described by a single-mode Maxwell model. Figure 11.4 shows the frequency dependence of the dynamic modulus for a 1 wt% C24HEUR aqueous solution.

The curves are the calculated results using the Maxwell model (Eqs. 11.2 and 11.3).

$$G' = G_0 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (11.2)$$

$$G'' = G_0 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (11.3)$$

$G'$  and  $G''$  are storage and loss moduli, respectively.  $G_0$ ,  $\omega$ , and  $\tau$  are equilibrium modulus, angular velocity, and relaxation time, respectively. A HEUR solution has a single relaxation time, i.e., it exhibits elastic (rubber-like) properties under rapid deformation, yet it flows under slow deformation. The relaxation time of a HEUR solution depends on the length of the middle chain and the size of its hydrophobic



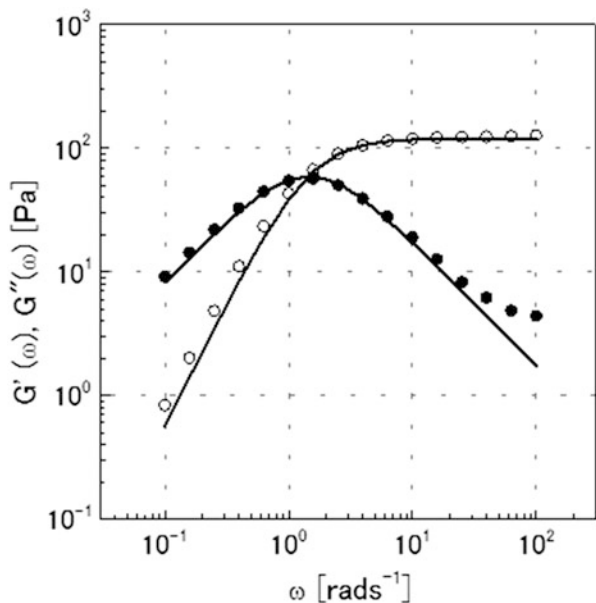
**Fig. 11.3** Size distributions, obtained from DLS, for various concentrations of C24HEUR. The weight percentage of polymer and the mean hydrodynamic radius are indicated

residues. Tanaka and Edwards [35] devised the transient network theory to explain this behavior. The relaxation time of a HEUR hydrogel is strongly related to the lifetime of flower micelles formed from HEUR molecules [35, 36].

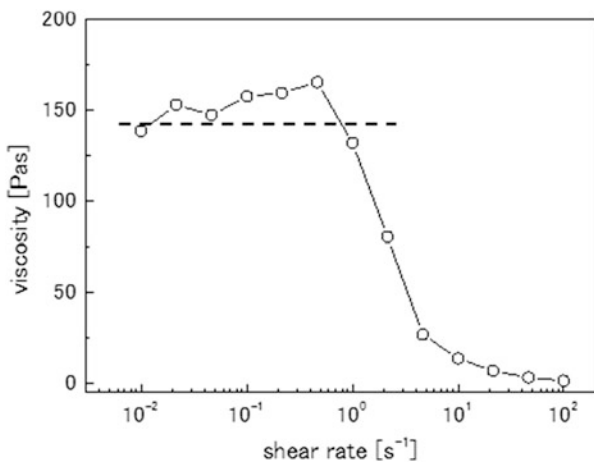
The steady-state flow behavior of an aqueous solution of HEURs is also unique. The steady-state flow curve for a 1.5 wt% C24HEUR aqueous solution is shown in Fig. 11.5

As mentioned above, Fig. 11.5 shows the initial shear thickening at low shear rates, followed by shear thinning at higher shear rates (the dotted line in the figure is an eye guide). In particular, the viscosity drops abruptly after peak shear thickening. According to modified transient network theory, this phenomenon is due to the nonlinear stretching effect of the effective chains in the transient network. Moreover, in this situation, it is expected that shear banding occurs [36].





**Fig. 11.4** The dynamic modulus against frequency for a C24HEUR 1 wt% aqueous solution. *Open circles* and *closed circles* denote storage and loss modulus, respectively. The *curves* denote the prediction of a Maxwell model (Eqs. 11.2 and 11.3)



**Fig. 11.5** Flow curve for C24HEUR 1.5 wt% aqueous solution (The *dotted line* is an eye guide as the zero-shear viscosity)

### 11.3.3 *Nonlinear Flow Properties for C24HEUR Under Large Deformation*

Recently, studies of the behavior of HEUR under large deformations have been reported [4, 12]. Because the “first feeling” for cosmetics is related to start-up flow, we focused in these nonlinear rheological properties for aqueous HEUR solutions. When these viscoelastic fluids are used in cosmetics, their rheological behavior under large deformations must be considered because, under typical usage, cosmetics are subject to large deformation. As an example of nonlinear deformation, stress growth behavior under the step shear flow was examined.

In general, the stress under a certain strain is defined by the balance of the tensile strength between the end of the active chain and the lifetime and dissociation rate of the transient cross-link point. If the tension and the dissociation rate for the system can be estimated, the mechanical properties can also be estimated. In particular, the behavior in the nonlinear region is quite interesting [25, 26].

The shear stress growth behavior can be modeled by Eq. 11.4:

$$\eta^+(t) = \eta^{(1)}t + \eta^{(2)}\frac{t^2}{2!} + \eta^{(3)}\frac{t^3}{3!} + \dots \quad (11.4)$$

Here  $\eta^{(1)}$ ,  $\eta^{(2)}$ , and  $\eta^{(3)}$  can be explained as follows:

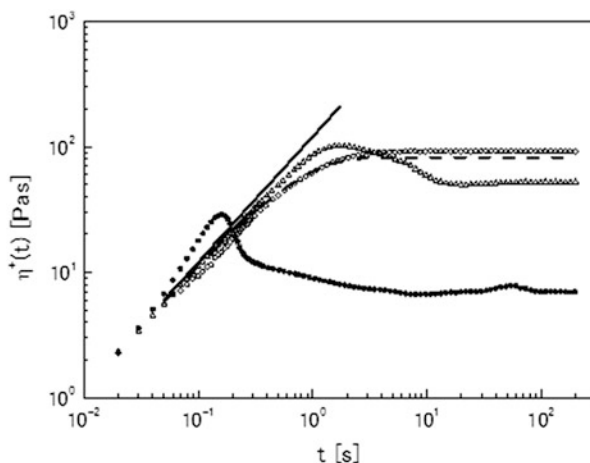
$$\eta^{(1)} = G'(\omega \rightarrow \infty) \quad (11.5)$$

$$\eta^{(2)} = -\lim \omega G''(\omega) \quad (11.6)$$

$$\eta^{(3)} = -(A + B\dot{\gamma}^2) \quad (11.7)$$

The third coefficient is dependent on the shear rate. In particular, coefficient  $B$  includes a factor showing the effect of nonlinear stretching of the elastic active chains. If the factor is equal to zero, the chain reduces to a Gaussian series and  $B$  becomes zero. In other words, any unusual behavior during the time scale is contained in the third term of Eq. 11.4. The dynamics of the network contains the effect of nonlinear stretching, and this nonlinear stretching effect can be observed as an unusual increase in the viscosity growth curve under the initial shear flow.

Here, we will introduce a typical example of this unusual increase in stress. The viscosity growth curves for a 1.5 wt% C24HEUR aqueous solution at several shear rates are shown in Fig. 11.6. Because, in a transient network, stress under a particular level of strain is determined by the balance between the tension between the ends of the active chains and the lifetime dissociation rate of the transient cross-link points [25, 26], the viscosity growth curve was checked at three constant shear rates. For easier comparison of samples, we have introduced the concept of normalized shear



**Fig. 11.6** Viscosity growth curves for a C24HEUR 1.5 % aqueous solution. *Open circles, squares, and closed circles* denote the results at  $W_i = 0.1, 1.0,$  and  $10,$  respectively. The *solid line and dotted line* denote the elastic response at very short time periods (Eq. 11.8) and expected viscosity growth curve estimated by Eq. 11.9, respectively

rare,  $\dot{\gamma}\tau$ . The open circles, open squares, and closed circles in Fig. 11.6 denote the viscosity growth curves for  $\dot{\gamma}\tau = 0.1, 1.0,$  and  $10,$  respectively. The solid lines denote the linear elastic response calculated using the following equation:

$$\eta = G_0 t \quad (11.8)$$

The dotted lines denote the viscoelastic response predicted by the Maxwell model, as described in Eq. 11.9:

$$\eta^+(t) = G_0 \tau \left[ 1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (11.9)$$

An upturn in stress is clearly evident for the curve under highest shear rate flow.

As shown, a stress upturn, which is the overshoot from the elastic response according to Eq. 11.8 (the straight line in Fig. 11.6), appears at high shear rate flow ( $W_i = 10$ ). It is interesting to consider the influence of this unusual increase in stress on the “primary feeling” because consumers may sense this unusual response when they start to spread the cosmetic product on their skin. This may be felt as an initial resistance followed by decreasing resistance. Therefore, C24HEUR is a promising rheology control agent not only because of its acid resistance but also because of its preferable usage feeling.

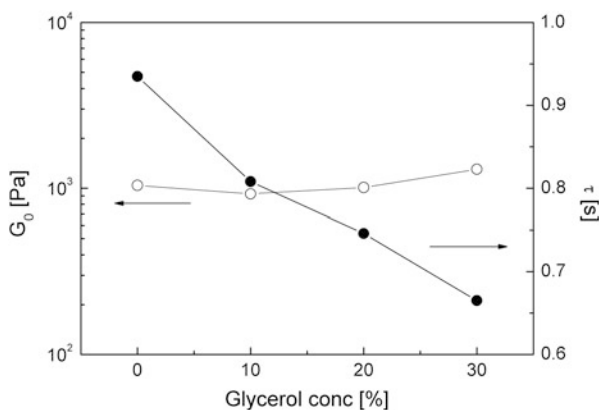
Concerning cosmetic applications, the effect of the various additives on the rheological properties of products must be examined because, generally, cosmetics contain a variety of ingredients. In particular, alcohols and polyols are important ingredients, used as preservatives and emollients. As mentioned above, the

mechanical properties of the transient networks in HEUR hydrogels are strongly related to the physicochemical properties of the formed micelles, that is, the cross-links formed in the hydrogels. Therefore, the effects of these additives on the rheological properties of HEUR aqueous solutions must be investigated, in particular, their nonlinear flow behavior. Therefore, we will discuss studies on the effects of additive glycerol [22] and methanol [23].

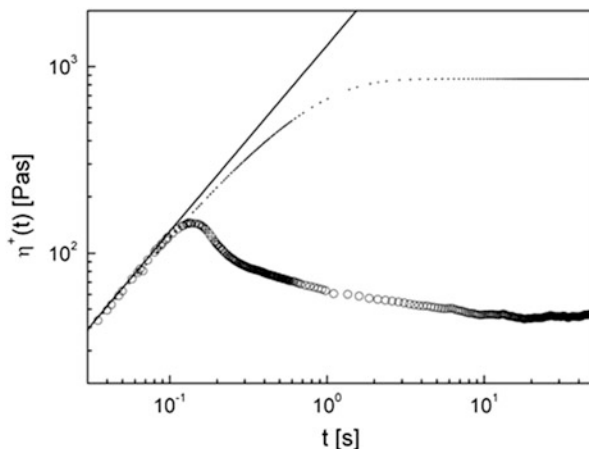
### 11.3.4 Effect of Glycerol on the Rheological Properties of C24HEUR

Figure 11.7 shows the dependence of the mechanical characteristics on C24HEUR hydrogels on the glycerol concentration. Upon addition of glycerol, the relaxation time shortened. In contrast,  $G_0$  slightly increased with increasing glycerol concentration. This result suggests that glycerol affects the structure of the polymer network at high concentrations. The effects of glycerol on the micellar structure of a nonionic surfactant [32] and PEO-PPO-PEO block copolymers [1] have been reported. In general, upon addition of glycerol, PEO chains shrink as a result of dehydration. From linear viscoelastic measurements, glycerol seems to change the cross-link points of the transient network. As shown in Fig. 11.7, shorter relaxation times reduce the duration that the hydrophobic end chains of C24HEUR remain at the micellar junctions.

The effect of glycerol on the viscosity growth behavior of aqueous solutions of C24HEUR at 3 wt% containing 30 wt% glycerol is shown in Fig. 11.8. Because the



**Fig. 11.7** Variation of estimated equilibrium shear modulus ( $G_0$ ) and relaxation time ( $\tau$ ) vs. glycerol concentration. *Open and closed symbols* denote  $G_0$  and  $\tau$ , respectively (From Ref. [22], with permission from Springer)



**Fig. 11.8** The viscosity growth curves at various shear rates for a C24HEUR 3 wt% aqueous solution containing 30 wt% glycerol at  $10 \text{ s}^{-1}$ . The lines and dotted lines denote the elastic response at very short time periods (Eq. 11.8) and expected viscosity growth curve estimated by Eq. 11.9, respectively

relaxation times for these samples are approximately 0.7 s, values of  $W_i$  are greater than one.

The unusual increase in stress shown in Fig. 11.6 is not present in the sample containing 30 wt% glycerol. This indicates that glycerol affects the dynamics of the network, particularly the mechanical response of the active chains in the networks. Furthermore, the disappearance of the unusual upturn in stress means that the sample containing 30% glycerol does not involve nonlinear stretching. As mentioned above, glycerol reduced the relaxation time. Consequently, we believe that glycerol affected the structure of the cross-links of the transient network in this system. Moreover, glycerol affected the manner of nonlinear deformation. A possible hypothesis is described as follows: because glycerol is a water-soluble solvent containing three hydroxyl groups, it may affect the hydration of the hydrophilic chains of C24HEUR, that is, the PEO chains. In the presence of a small amount of water-miscible solvent, a cononsolvency effect occurs [17, 19, 37, 39, 40]. Consequently, polymers shrink as a result of dehydration. If the active chains, connected at both ends to the cross-link point, shrink, the active chains between the cross-link points collapse. When shear flow is applied to the system, the collapsed chains reel out. Because the polymer chains are reeled out, they cannot be further stretched. Therefore, samples containing high concentrations of glycerol do not show the unusual increase in stress.

### 11.3.5 Effect of Methanol on the Rheological Properties of C24HEUR

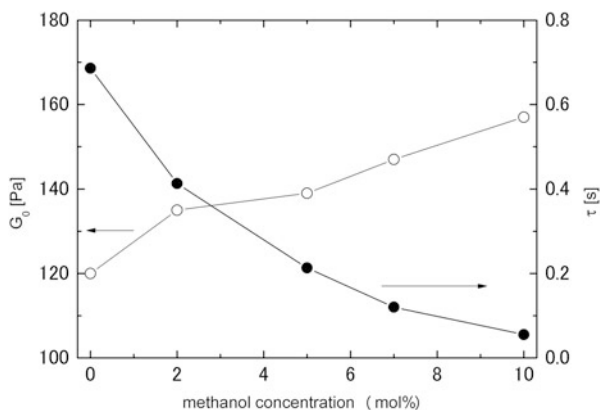
Methanol also affects the rheological properties of aqueous solutions of C24HEUR [23], and Fig. 11.9 shows the dependence of the linear viscoelastic characteristics of these solutions on the methanol concentration.

In this case, the polymer concentration was fixed at 1.5 wt%. These results show that addition of methanol both reduces the relaxation time and increases  $G_0$ , with  $G_0$  increasing slightly with methanol concentration. The relaxation time behavior is similar to that induced by the addition of glycerol, although the effect of  $G_0$  is different. According to the classical theory for gels, the modulus of a gel is given simply by the following equation, Eq. 11.10:

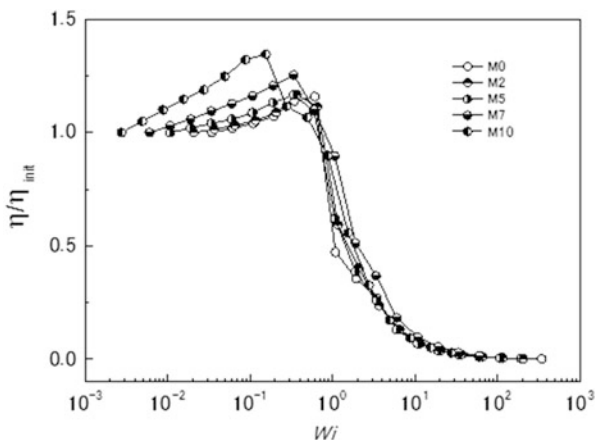
$$G = \nu k_B T \quad (11.10)$$

$\nu$  is the number of effective chains in the gel network,  $k_B$  is the Boltzmann constant, and  $T$  is temperature. Because our polymer concentration was constant (1.5 wt%), the  $G_0$  behavior suggests that the number of effective chains in the gel network increases when methanol is added. This may be because methanol reduces the aggregation number of the flower micelles.

Because the steady-state flow behavior changes with micelle properties, the addition of methanol is expected to affect the steady-state flow curve. We determined the steady-state viscosity at various shear rates in the range 0.05–500  $\text{s}^{-1}$  for samples containing methanol (0–10 mol%). We analyzed our data in terms of normalized viscosities,  $\eta/\eta_{\text{init}}$ , and normalized shear rates,  $\dot{\gamma}\tau$ , where  $\eta_{\text{init}}$  is the viscosity measured at 0.05  $\text{s}^{-1}$  and  $\tau$  is obtained from measurements of dynamic



**Fig. 11.9** Variation of estimated equilibrium shear modulus ( $G_0$ ) and relaxation time ( $\tau$ ) vs. methanol concentration. *Open and closed symbols* denote  $G_0$  and  $\tau$ , respectively (From Ref. [23], with permission from Springer)



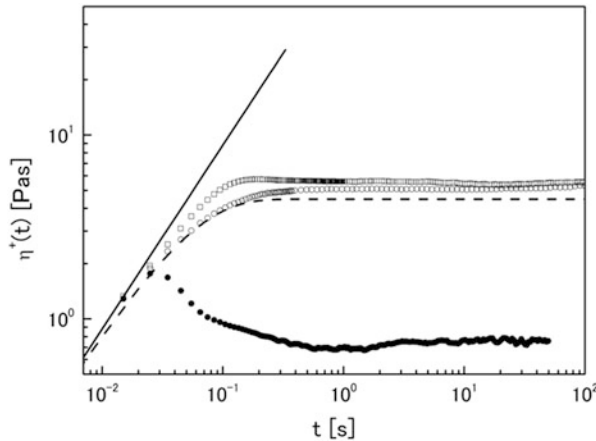
**Fig. 11.10** Flow curves for C24HEUR 1.5 wt% solutions containing methanol in concentrations ranging from 0 to 10 mol% (M0, M2, M5, M7, and M10). Normalized viscosity and shear rate are employed in the coordinate system. Viscosity is normalized as  $\eta/\eta_{\text{init}}$ , which is the apparent viscosity at  $0.05 \text{ s}^{-1}$ . Shear rate is shown as Weissenberg number ( $Wi = \tau \dot{\gamma}$ ). The values of  $\tau$  for these samples were estimated by a Maxwell model (Eqs. 11.2 and 11.3) (From Ref. [23], with permission from Springer)

moduli. Such a normalized coordinate system enables the comparison of the shear-thickening behavior at different methanol concentrations.

Figure 11.10 shows flow curves (normalized viscosity,  $\eta/\eta_{\text{init}}$ , vs. normalized shear rate,  $\dot{\gamma}\tau$ ) for the measured samples. The labels, M0, M2, M5, M7, and M10, denote the methanol concentration (mol%) in each sample. The normalized viscosity increases gradually at first; then, at a normalized shear rate  $< 1$ , it decreases abruptly. The intensity of shear thickening ( $\eta/\eta_{\text{init}}$ ) depends on methanol concentration and becomes quite significant. Moreover, the viscosity peak shifts to a shorter time (lower shear rate) with increasing methanol concentration. Although shear-thickening behavior is affected by methanol concentration, the shear-thinning behavior of the samples at flow rates above the critical shear rate is similar, and the flow curves of the samples essentially overlap beyond  $\dot{\gamma}\tau = 1$ . This phenomenon is expected, and we speculate that it is caused by shear-banding transitions.

The unusual stress increase that occurs at the step shear flow shown in Fig. 11.6 disappears on addition of both methanol and glycerol. Figure 11.11 shows the viscosity growth curve for C14HEUR 1.5 wt.% solution containing 10 mol% of methanol.

The origin of this phenomenon is as the same that for glycerol. As shown in Fig. 11.8, the effect of glycerol is similar to that of methanol concerning relaxation time, in particular, concerning the lifetime of the temporary cross-link points. Therefore, methanol also affects the properties of the cross-link point and the elastic active chains.



**Fig. 11.11** Viscosity growth curves for a C24HEUR 1.5 % aqueous solution containing 10 mol% methanol. *Open circles, squares, and closed circles* denote the results at  $W_i = 0.1, 1.0,$  and  $10,$  respectively. The *solid line and dotted line* denote the elastic response at very short time periods (Eq. 11.8) and expected viscosity growth curve estimated by Eq. 11.9, respectively (From Ref. [23], with permission from Springer)

## 11.4 Water-Swellable Microgel

Microgels are promising candidates for cosmetic rheology control agents that do not cause undesirable usage feelings such as the “sticky after feeling” or “spinability” (see Sect. 11.2). Carbopol is one of the most famous microgel-type rheology control agents for cosmetics [10, 38]. However, this class of cross-linked polyacrylates has several issues that must be overcome. The most serious issue is their pH dependence because Carbopol contains carboxyl groups in its main chains, and it forms transparent gels only under alkali conditions, thus reducing the formulation options for cosmetics. One solution for this issue is the application of neutral polymer microgels. For example, agar microgels have been used in cosmetics [16]. However, agar microgels have unsatisfactory usage feelings due to their poor swelling and brittle mechanical properties.

Polyacrylamides are considered to be suitable polymers for cosmetic rheology control agents due to their usage feeling. Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) is an interesting monomer. Because the monomer is sulfonic acid, a polymer copolymerized with AMPS can swell over a wide pH range. In fact, several kinds of copolymers that incorporate AMPS have been developed as cosmetic rheology control agents [13–15].

However, a problem exists, that is, how to polymerize microgels incorporating AMPS? Polymer microgels are commonly prepared by either emulsion polymerization or precipitation polymerization. However, because both AMPS and the resultant polymer are soluble in water, it is difficult to employ precipitation polymerization.



Moreover, AMPS is practically insoluble in organic solvents; consequently, emulsion polymerization cannot be used.

To make water-swellaible polyAMPS microgels, we have developed a novel inverse microemulsion polymerization (IMEP) system [18]. It is well known that a ternary system using a nonionic surfactant exhibits a “phase inversion phenomenon.” The temperature at which the phase inversion occurs is called the hydrophilic-lipophilic balance (HLB) temperature. A transparent and low viscosity phase appears in the vicinity of this temperature. The phase is an O/W microemulsion ( $W_m$ ) or W/O microemulsion ( $O_m$ ). Because  $O_m$  consists of reverse micelles, swollen by water, this phase can be used as a polymerization “container” for polymers containing AMPS. Moreover, since the  $O_m$  phase is determined by both the composition of the system and the temperature, it is easy to control the size of the “container.” Therefore, the size of the swellaible microgels can be controlled to be very small, almost the same size as that of the microemulsion particles.

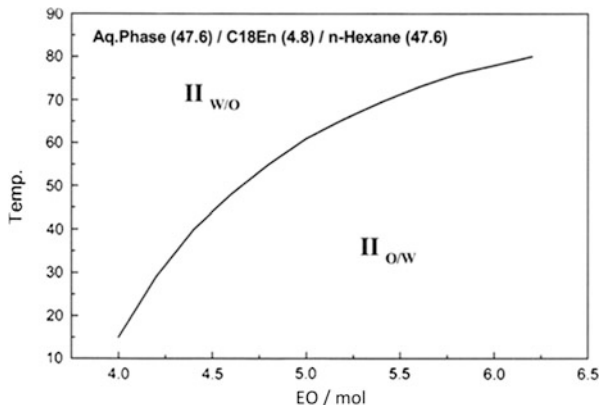
### ***11.4.1 Inverse Microemulsion Polymerization System***

To characterize the pseudo-ternary system consisting of a monomer aqueous solution, nonionic surfactant, and n-hexane, a phase diagram study was performed. The aqueous phase, monomer solution consisted of dimethylacrylamide (DMAA) and AMPS. The monomer concentration of the aqueous phase was 20 wt%, and the molar mixing ratio of DMAA and AMPS was 80:20. The weight ratio of the aqueous phase and n-hexane was 50:50. The surfactant was added at 5 % of the total weight of the system. C18E<sub>n</sub>-type nonionic surfactants were used in the study. Here, *n* indicates the mean stoichiometry of ethylene oxide, which ranged from 4 to 6 M. The *n* value was adjusted through variation of the mixing weight ratio of C18E3 and C18E6, which are industrial grade surfactants. The phase inversion temperatures of the systems were determined by conductivity measurements. The phase diagram is shown in Fig. 11.12.

The curve in Fig. 11.12 indicates the phase inversion temperature. The system was observed to be transparent and had low viscosity at around this temperature. This implies that the reversed micelle solution phase exists at this temperature. From this result, we can construct an inverse microemulsion polymerization system. If the temperature for the polymerization is known, the components of the pseudo-ternary system can be adjusted to yield the desired HLB temperature. For example, if we want to perform a thermal radical polymerization at 65 °C, the necessary surfactant is C18E5.

We polymerized water-swellaible microgels consisting of DMAA and AMPS with additional methylenebisacrylamide (MBA) as a cross-linker. In this section, these microgels are labeled as D-A microgels.

**Fig. 11.12** The phase diagram of the pseudo-ternary inverse microemulsion polymerization system. The composition ratio of the system is shown in the panel. The curve shows the phase conversion temperature (From Ref. [18], with permission from Elsevier)



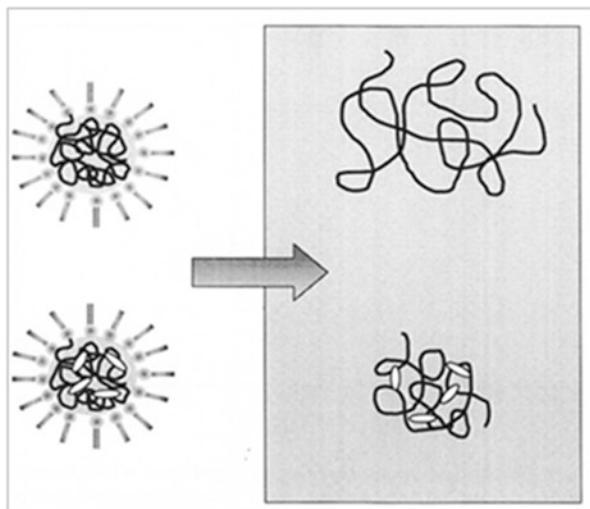
### 11.4.2 Spherical Shape of the Water-Swellable Microgels Polymerized in a Confined Space

To produce a favorable “primary feeling,” skin-care cosmetic products must have “body” under low deformation speeds, yet they should flow easily under higher deformation speeds, as mentioned in Sect. 11.2. If sufficient microgel is added to the aqueous phase of an emulsion, percolation through the microgels gives “body” to the emulsion; moreover, the resultant product gains shear-thinning, non-Newtonian flow properties if the microgel particles are sufficiently soft. As an initial step in the study of the rheological properties of water-swellable microgels, we investigated the properties of dilute microgel solutions.

It is important to know the critical volume fraction at which the microgels form a percolating network in aqueous solution. Because the microgels swell greatly in aqueous systems, it is difficult to estimate their volume fraction from the weight ratio (concentration). However, the intrinsic viscosity can be used. The intrinsic viscosity is a characteristic concerning the spatial size of colloidal particles and is defined by Eq. 11.11:

$$[\eta] = \lim_{c \rightarrow 0} \frac{(\eta - \eta_s)}{c\eta_s} \quad (11.11)$$

$\eta$  is the viscosity of the microgel dispersion,  $\eta_s$  is the viscosity of the solvent, and  $c$  is the microgel concentration. We measured the intrinsic viscosities in 3 mM sodium chloride aqueous solution for a series of cross-linked DMAA-AMPS copolymers, which were polymerized in aqueous solution and IMEP. The intrinsic viscosity of the microgels polymerized in solution was ca. 25 dL/g. In contrast, for microgels polymerized in IMEP, it was ca. 7 dL/g, indicating that the cross-linked polymers polymerized in IMEP, that is, a confined space, were more compact than those polymerized in solution. A conceptual scheme is shown in Fig. 11.13.



**Fig. 11.13** Conceptual illustration for polymerization in a confined space (From Ref. [18], with permission from Elsevier)

### 11.4.3 Flow Behavior of the Microgel Dispersions

To understand the overlap concentration ( $c^*$ ) for the microgels, the relationship between the relative viscosity and the microgel concentration was studied. The microgel concentration was normalized by its  $[\eta]$  value. Generally,  $[\eta]$  is related to  $c^*$  and the volume fraction occupied by colloidal particles, ( $\phi$ ), by assuming that the colloidal particles behaving as impenetrable spheres according to Eq. 11.12:

$$\frac{\eta}{\eta_s} = 1 + 2.5\phi \quad (11.12)$$

From Eqs. 11.11 and 11.12, the relationship between  $[\eta]$  and  $\phi$  is given by the following equation:

$$[\eta] = \frac{2.5\phi}{c} \quad (11.13)$$

Because it is expected that spherical colloid particles begin to overlap when  $\phi$  is around 0.4,  $c^*$  can be described as follows:

$$c^* \approx \frac{1}{[\eta]} \quad (11.14)$$

The inflection point in the viscosity versus the concentration plot is considered to be  $c^*$ .

**Fig. 11.14** Concentration dependency of the relative viscosities for D-A microgel dispersions at various concentrations ranging from  $c[\eta] = 0.4$  to 2.6 (From Ref. [20], with permission from Elsevier)

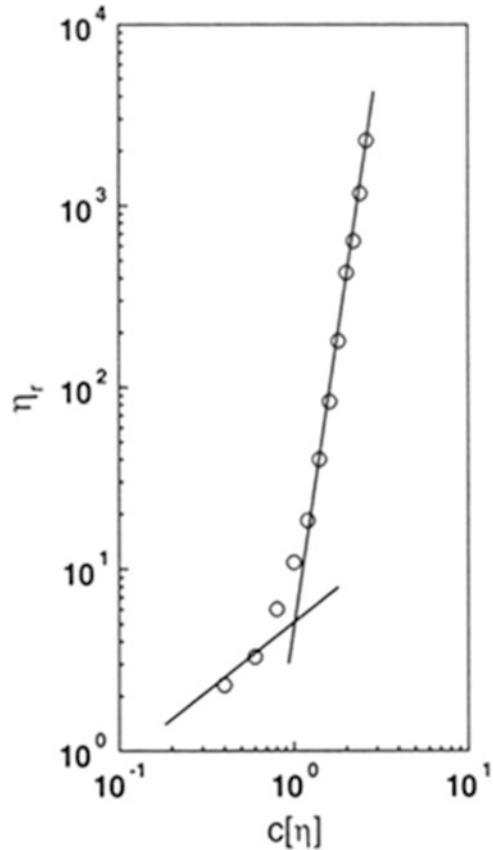
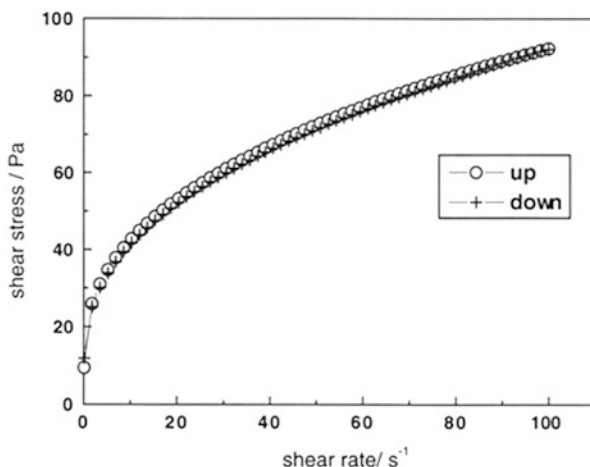


Figure 11.14 shows the relationship between the relative viscosities and the normalized microgel concentration, ( $c[\eta]$ ). It is clear that the inflection point is at around  $c[\eta] = 1$ . This indicates that the microgels can be considered as hydrodynamically impenetrable spheres and that, as such, the impenetrable spheres do not have dangling chains.

#### 11.4.4 Shear-Thinning, Non-Newtonian Flow of the Microgel Dispersions

The yield stress is one of the important rheological properties for “primary feeling” of skin-care cosmetics (see Sect. 11.2.1). We investigated the yielding properties from the steady-state flow curve. A typical flow curve for an aqueous dispersion of a microgel is shown in Fig. 11.15. The flow curves show that the aqueous dispersions of the microgel exhibit pseudoplastic flow, that is, they have finite



**Fig. 11.15** Hysteresis of the flow curve for the D-A microgel dispersion. The concentration of the sample was  $c[\eta] = 2.0$ . Circles and crosses denote upward and downward procedures, respectively (From Ref. [20], with permission from Elsevier)

yield stresses and exhibit shear-thinning flow. The circles and crosses denote the results for the upward (increasing shear stress) and downward (decreasing shear stress) procedures, respectively. Although most condensed colloidal dispersions show hysteresis, in this case, there is none. The lack of hysteresis may be due to the softness of the microgel particles.

To estimate the yield stress from the flow curve, we used the Herschel-Bulkley equation, an empirical power-law equation.

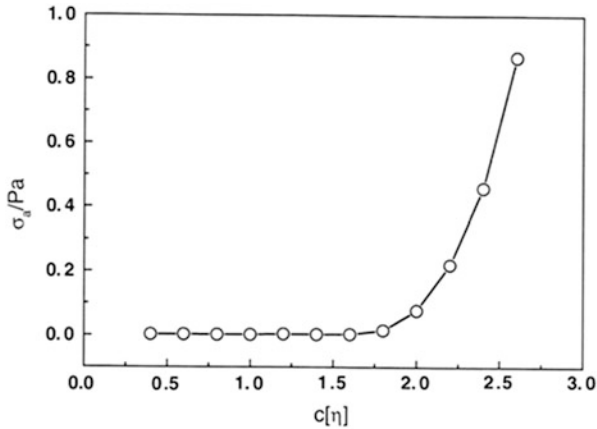
$$\sigma = \sigma_y + k(\dot{\gamma})^n \quad (11.15)$$

$\sigma$  and  $\dot{\gamma}$  are the shear stress and shear rate, respectively. The three parameters are characteristic of non-Newtonian flow, and  $k$  is a consistency parameter,  $\sigma_y$  is yield stress, and  $n$  is the H-B index. This empirical power-law model has been used in various studies [16, 18, 34].

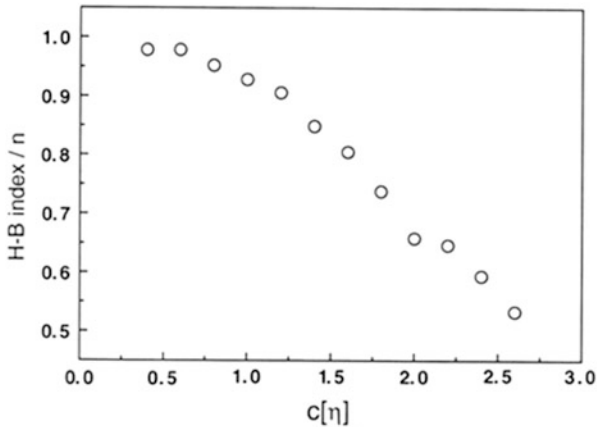
This empirical equation is useful for analysis of this type of flow curve. The relationship between the yield stress and  $c[\eta]$  is shown in Fig. 11.16.

The yield stress increases above  $c[\eta] = 1.8$ . The volume fraction occupied by the microgels for this concentration is 0.72, derived from Eq. 11.13. If the particles are hard spheres, the dispersion has infinite viscosity at around  $\phi = 0.5$ , the random close packing limit. A value of 0.72 means that the microgels packed each other with large deformation. Because the microgel was only slightly cross-linked (0.5 mol% of MBA was copolymerized), the microgels may become progressively deformed as the microgel concentration increases. Also, this is likely to be the apparent yield stress due to the friction between microgel particles.

The H-B index is also interesting concerning the flow properties, in particular, the shear-thinning behavior. Shear-thinning behavior is associated with  $0 < n < 1$  and the

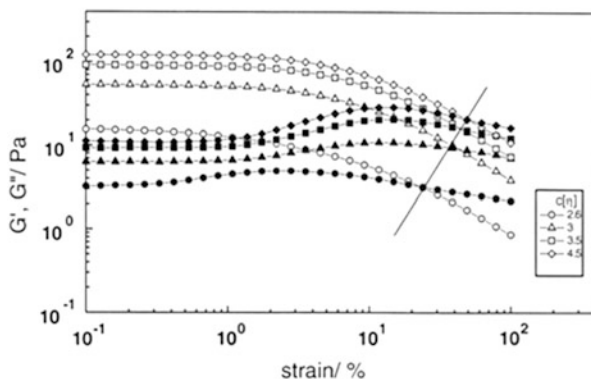


**Fig. 11.16** Concentration dependence of the apparent yield stress evaluated from Eq. 11.15 for the A-D microgel dispersions (From Ref. [20], with permission from Elsevier)



**Fig. 11.17** Concentration dependence of the H-B index evaluated by Eq. 11.15 for the A-D microgel dispersions (From Ref. [20], with permission from Elsevier)

unusual shear-thickening behavior at  $n > 1$ . Figure 11.17 shows the concentration dependence of  $n$  for the aqueous microgel dispersions. It shows that  $n$  for the lower concentration samples is nearly 1, indicating the samples almost behave as Newtonian fluids. However, at higher concentrations, the value  $n$  becomes smaller, eventually becoming close to 0.5, according to the Casson's theory for spherical particle dispersions. Interestingly, the relationship between the food texture and H-B index shows that foods having a “fresh” texture, such as tomato juice, have  $n = 0.5$ . Therefore, a cosmetic product that has  $n = 0.5$  can be expected to have a “fresh” primary feeling [16].



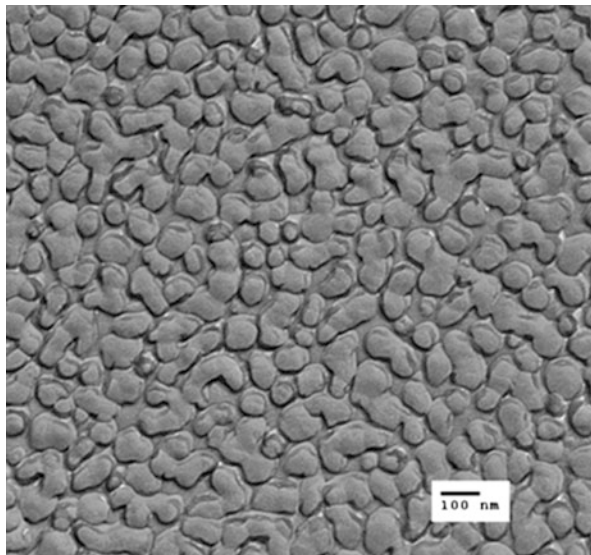
**Fig. 11.18** Strain dependence of the shear modulus for the A-D microgel dispersions. *Open and closed symbols* denote storage and loss modulus, respectively. All measurements were performed at 1 Hz (From Ref. [20], with permission from Elsevier)

Shear-thinning non-Newtonian flow properties for water-swollable microgels consisting of DMAA-AMPS, described above, strongly contribute to the “primary feeling” of skin-care cosmetic products. In particular, because the microgels are polymerized in a confined space, the swollen shape is expected to be spherical, as shown by several measurements. Furthermore, these microgels have a distinct “primary feeling” that stands out from the other rheological control agents.

### 11.4.5 Condensed Microgel Aqueous Dispersions

The yielding behavior of condensed microgel dispersions can also be studied by dynamic viscoelasticity measurements [20]. The dynamic modulus for D-A microgel aqueous dispersions during strain-sweep measurements is shown in Fig. 11.18. The storage modulus ( $G'$ ) is always larger than loss modulus ( $G''$ ) in the linear viscoelastic region. Although the microgels in the dispersion are essentially discrete, the condensed dispersion acts as a continuous network structure. The condensed microgel dispersion, which appears as a “bulk gel,” collapses under large shear strains. The crossover point of  $G'$  and  $G''$  is one of the criteria for this collapse. The solid line denotes the crossover point for the dispersion at various concentrations ranging from  $c[\eta] = 2.5$  to 4.5. The shear strain at collapse points is around 10%. The values are somewhat larger than a condensed emulsion or dispersion that consists of hard spheres, and this may be due the “softness” of the microgels.

It is shown that D-A microgels are closed packing and they behave like “bulk gels” in highly concentrated dispersions. We attempted to observe this close packing using electron microscopy [21]. The freeze-fracture transmittance electron microscopy (FF-TEM) method is good for such wet samples. Figure 11.19 shows



**Fig. 11.19** Freeze-fracture TEM image of the A-D microgel dispersion ( $c[\eta] = 3.0$ )

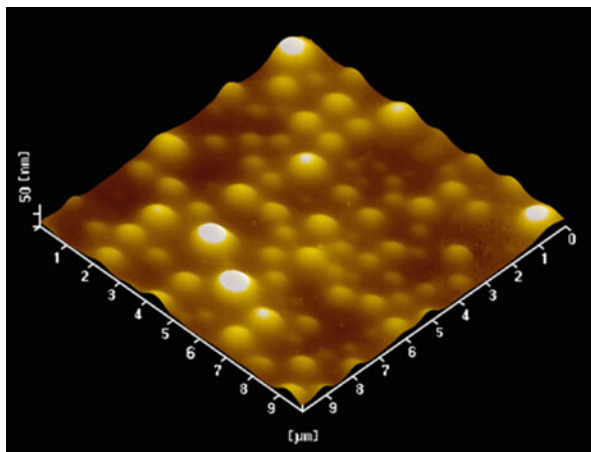
an FF-TEM image of the microgel aqueous dispersion ( $c[\eta] = 14$ ). It is clear that the microgels are packed with deformation.

The condensed state of the D-A microgels after drying was also observed by atomic force microscopy (AFM). A small amount of the aqueous A-D microgel dispersion was spread on a mica plate and dried for 18 h at room temperature. The dried sample was observed by AFM, as shown in Fig. 11.20. Dome-shaped projections are visible in the image, indicating that the shapes of the microgel particles in aqueous dispersion, shown in Fig. 11.19, are retained after drying. Therefore, when a cosmetic product containing the microgels is applied to the skin, the surface of the skin may show this uneven shape after evaporation of moisture. It is well known the frictional resistance of uneven surfaces is smaller than that of flat and smooth surfaces. Therefore, the surfaces observed in Fig. 11.20 may influence the “after feeling” of cosmetic products comprising A-D microgels. Moreover, the observed uneven surface means that the microgels are swollen even after drying for 18 h. Consequently, we expect that the swollen microgels would function well as a moisturizing agent because the swollen microgels may supply necessary moisture to the stratum corneum.

## 11.5 Summary

Because the 3D structures formed in aqueous solutions of C24HEUR are temporary, they dissociate easily under deformation; however, hydrogels consisting of C24HEUR have “body” in their resting state. The aqueous solution of C24HEUR





**Fig. 11.20** AFM image of the A-D microgel in the dry state

exhibits shear-thinning, non-Newtonian flow: a desirable feature for a cosmetic rheology control agent. Moreover, because the main part of the polymer is comprised of polyethyleneoxide, a nonionic polymer, the polymer has both acid and salt resistance.

Unusual nonlinear flow properties, the topic of this section, namely, the unusual stress upturn under step shear flow, are interesting because friction at the start of rubbing is expected to be related to the “primary feeling.” However, it should be noted that, in some cases, coexisting ingredients may affect these features.

A novel microgel that can be swollen, even in acidic aqueous phases, has been developed. The microgel exhibits excellent performance as a cosmetic rheology control agent not only compensating for the disadvantages of existing ingredients. In particular, because the microgels are polymerized in a confined space, they have a completely spherical shape, and this shape is the origin of its unique features as a cosmetic rheology control agent.

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