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# Magnetorheological Fluids Based on Associating Polymers

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**Summary:** Magnetic fluids based on associating polymers were prepared by ultrasonic dispersing of magnetite microparticles in aqueous solutions of hydrophobically modified polyacrylamides. It was shown that the magnetic fluids containing 1–3 vol.% of $Fe_3O_4$ microparticles can be reversibly transformed to physical gels under the action of magnetic field.

**Keywords:** associating polymers; magnetic fluids

## Introduction

Over the past decade, new functional smart polymer systems that are responsive to external stimuli have been extensively developed.[1–3] The stimuli can be diverse, they include temperature, pH, solvent and ionic composition, electric and magnetic field etc. To get magnetosensitive properties magnetic filler particles (MP) are usually introduced into polymer systems.[4–8] As an example one can cite magnetorheological fluids (MF) representing a suspension of micron-sized magnetic particles in polymer solution. For the preparation of MF various polymers were used.[8] In particular, Viota et al. investigated MF based on polyacrylic acid (PAA) solutions.[6] The best conditions to obtain stable suspensions were found for PAA with molecular weight of $3 \cdot 10^6$ g/mol at concentration about 1 g/l. The introduction of few hydrophobic groups into polyelectrolyte chains permits to get associating polyelectrolytes, which possess much higher viscosity in semidilute solutions in comparison with their non-modified counterparts. In this case the stabilization of MP can be achieved at much lower molecular weight or concentration of polymer. Recently, we have reported[8,9] the preparation of highly stable MF based on magnetite, maghemite and cobalt ferrite microparticles stabilized in aqueous solutions by charged hydrophobically modified polyacrylamides (HM PAAms), the molecular weight of which was two times smaller than that of PAA used by Viota. These HM PAAms are terpolymers containing three types of repeat units: (1) uncharged hydrophilic acrylamide (AAm) monomer units, (2) charged hydrophilic sodium acrylate (SA) units and (3) hydrophobic N-dodecylacrylamide (DDAAm) units. In this polymer, carboxylate groups of SA units anchor to anionic surface of MP, uncharged hydrophilic AAm units sterically stabilize MP against aggregation, whereas few hydrophobic DDAAm groups attracting each other facilitate the enhancement of viscosity of the system. This simple polymer allows independent tuning of the length of polymer chain, attachment density to the surface of MP, and hydrophobic interaction between different polymeric chains. Incorporation of MP into HM PAAm matrix can be carried out either by ultrasound treatment of a dispersion of MP in HM PAAm solutions or by synthesis of HM PAAm in the presence of MP.[8] In this paper, we report the rheological behavior of MF prepared by ultrasound dispersion of magnetite particles in HM PAAm aqueous

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solutions in dependence of MP size, polymer concentration and applied magnetic field.

## Experimental Part

The main characteristics of magnetite particles used in this work are presented in Table 1. MP1 sample was kindly provided by Dr. G.V. Stepanov (State Science and Research Institute of Chemical Technology of Organoelement Compounds, Moscow, Russia), whereas MP2 sample was purchased in FerroLabs Inc., USA.

HM PAAms were synthesized by micellar radical polymerization in water as described in detail in.[9–12] The molecular mass (MM) of HM PAAm was determined by the gel permeation chromatography as reported elsewhere.[13,14] The samples of HM PAAm are denoted like 1.0-C12/10SA, which indicates that the sample contains 1 mol.% of DDAAm units, 10 mol.% of SA units and 89 mol.% of AAm units. In some cases instead of SA we used acrylic acid (AA) units. The compositions and the molecular masses of the prepared HM PAAms are presented in the Table 2.

Viscoelastic behavior of MF was studied with the use of the rotational rheometer Rheostress RS 150L (Haake). Samples were placed in the measuring unit with the cone-plane configuration (the cone radius of 17.5 mm, the cone angle of 2°). Sample volume was equal to 0.3 ml. The measurements were performed at 20° ± 0.5°C in static and dynamic regimes. In static regime, the dependencies of the effective viscosity, $\eta$, on the shear stress were measured, the shear stress being varied from 0.05 to 1000 Pa. In the dynamic regime, the frequency dependencies of the storage modulus, $G'$, the loss modulus, $G''$, and the complex dynamic viscosity, $\eta^*$, were determined, the frequency being varied from $5 \cdot 10^{-3}$ to 30 Hz. The measurements were carried out in the region of linear viscoelasticity, when the modulus value does not depend on the amplitude of the deformation.

***Table 1.***
Characteristics of magnetite particles.

| Sample | Size of particles | Saturation magnetization | Residual magnetization | Coercive force |
|---|---|---|---|---|
| | μm | emu/g | emu/g | Oe |
| MP1 | 0,37 | 95 | 9,5 | 63 |
| MP2 [a)] | 3–5 | 120 | 1,4 | 12 |

[a)] MP were supplied as a suspension stabilized by sodium oleate in alkali medium, pH = 14, magnetite content is 20 vol.%.

***Table 2.***
Characteristics of HM PAAms.

| Sample | DDAAm | SA | AA | $C^{*a)}$ | $M_w \cdot 10^{-6}$ |
|---|---|---|---|---|---|
| | mol. % | mol. % | mol. % | g/dl | g/mol |
| 1.5-C12/10SA | 1.5 | 10 | - | 0.167 | 1.23 |
| 1.5-C12/15SA | 1.5 | 15 | - | 0.151 | 1.5 |
| 1.5-C12/20SA | 1.5 | 20 | - | 0.136 | 1.85 |
| 1.0-C12/10SA | 1.0 | 10 | - | 0.134 | 1.91 |
| 1.0-C12/10AA | 1.0 | - | 10 | 0.155 | 1.2 |
| 1.0-C12/15AA | 1.0 | - | 15 | 0.151 | 1.5 |
| 1.0-C12/20AA | 1.0 | - | 20 | 0.147 | 1.6 |
| 0.8-C12/10SA | 0.8 | 10 | - | 0.142 | 1.2 |
| 0.8-C12/10AA | 0.8 | - | 10 | 0.125 | 2.2 |
| 1.5-C12/10AA | 1.5 | - | 10 | 0.15 | 1.51 |

[a)] $C^*$ is the overlap concentration for coils of initial polyacrylamide defined as $C^* = M/(3/4\pi R^3 N)$, where M is the weight average molecular mass, R is hydrodynamic radius and N is the Avogadro number.

Rheological studies were performed both in the absence and in the presence of an external magnetic field. In the latter case, a permanent magnet with uniform magnetic field of 0,07 Tl was placed on a stationary bottom plate of the cone-plane measuring unit, so that the magnetic field was directed perpendicular to the shear stress. It was shown that the magnetic field was uniform with the accuracy of 97% in the whole volume of the samples.

## Results and Discussion

### Stability of MF

First, the stability of MF was studied at different concentrations of polymer and MP. The results are summarized in Tables 3 and 4. From Table 3 it is seen that at high content of MP (5 vol.%) and at low polymer concentration (1C*) most of the dispersions are unstable. Especially fast separation process proceeds in the case of bigger MP (MP2). At low polymer concentration (1C*) the most stable system was obtained in the case of HM PAAm 1.0-C12/10SA (Table 3).

A much higher stability of dispersion is observed at larger polymer concentration (2C*). From Table 4 it is seen that at this concentration of HM PAAm practically all dispersions containing 1 and 3 vol.% of magnetite independently of the size of the particles are stable and do not separate during long time. A more pronounced stability of MF at larger polymer concentration may be due to higher viscosity of the medium. As to polymer composition, Table 4 shows that the terpolymers 1.0-C12/10AA and 0.8–12/10AA give less stable dispersions than their analogs containing SA units. Therefore, the presence of charged carboxylate groups plays an important role in the stabilization of magnetite dispersions ensuring strong polymer interactions with oppositely charged surface of MP. The experiments show that the optimum composition of HM PAAm for the stabilization of MP in the range of polymer concentrations 1C*-2C* is 1.0-C12/10SA. This sample was used in the rheological measurements.

### Effect of Magnetic Particles on the Rheological Behavior of MF in the Absence of Magnetic Field

Frequency dependencies of G' of aqueous solutions of HM PAAm before and after magnetite addition are shown in Figure 1. It is seen that in the absence of an external magnetic field some drop of the storage and loss moduli is observed in the presence of MP. This effect is more pronounced at lower concentration of polymer. These results may be explained by the fact that

***Table 3.***
Stability of MF containing HM PAAm at a concentration of 1C* and 5 vol. % of MP.

| Polymer | MP 1 | MP 2 |
|---|---|---|
| 1.5-C12/10-20SA | Separation after 24 hours | Separation < 1 hours |
| 1.0-C12/10-20AA | Separation < 24 hours | Separation < 1 hours |
| 1.0-C12/10SA | Separation > 6 days | No Separation |
| 0.8-C12/10AA | Separation < 24 hours | Separation < 1 hours |
| 0.8-C12/10SA | Separation < 24 hours | Separation < 1 hours |

***Table 4.***
Stability of MF containing HM PAAm at a concentration of 2C* and 1 and 3 vol. % of MP.

| Polymer | MP1 | MP2 |
|---|---|---|
| 1.0-C12/10SA | No separation | No separation |
| 0.8-C12/10AA | Separation after 24 hours | Separation after 24 hours |
| 0.8-C12/10SA | No separation | No separation |
| 1.0-C12/10AA | Separation after 24 hours | Separation after 24 hours |

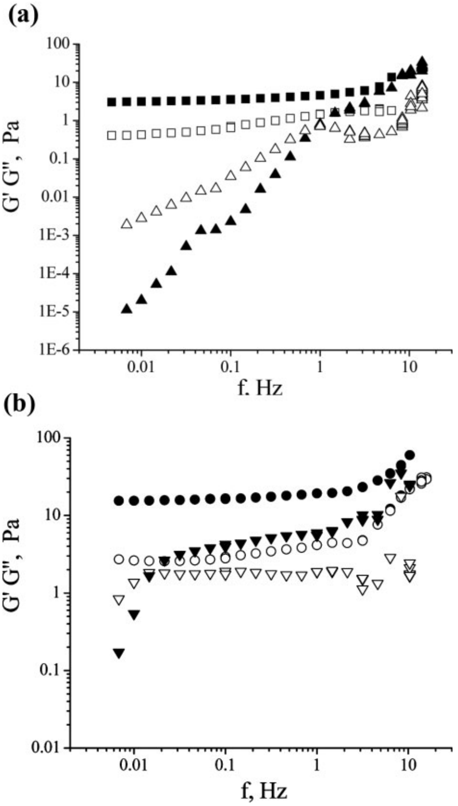

***Figure 1.***
Frequency dependencies of $G'$ (filled symbols) and $G''$ (open symbols) of aqueous solutions of HM PAAm 1.0-C12/10SA without magnetite and with 1 vol. % of MP2 in the absence of magnetic field. Polymer concentration is equal to 1C* (a) and 2C* (b); ■ - without MP, ▲ - with MP2, ● - without MP, ▼ - with MP2.

some polymer chains are adsorbed on the surface of MP, which reduces the amount of chains in the solution and therefore diminishes the average concentration of elastically active subchains.

## Effect of Magnetic Field on the Rheological Behavior of MF

Let us first consider the effect of magnetic field on the MF containing low concentration of polymer (1C*). In this case the behavior of the dispersion containing MP2 is close to Newtonian one, i.e. the viscosity is practically constant in the whole shear rate range (Figure 2). Its value is approximately equal to 0.05 Pa s. In a homogeneous magnetic field the viscosity increases by up to 6 orders of magnitude at low shear rate and demonstrates the shear-thining behavior.

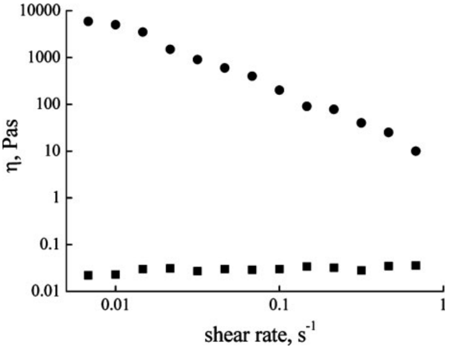

***Figure 2.***
Viscosity as a function of shear rate for aqueous solutions of HM PAAm 1.0-C12/10SA at polymer concentration of 1C* containing 1 vol.% of MP2; ■ = in the absence of magnetic field, ● = in magnetic field.

Simultaneously, the character of the frequency dependencies of the complex dynamic modulus components changes tremendously. From Figure 3 it is seen that in the absence of the magnetic field the dispersion behaves as a viscoelastic fluid: $G' < G''$ in a wide frequency ω range. At low frequencies $G'' \sim \omega$ and $G' \sim \omega^2$

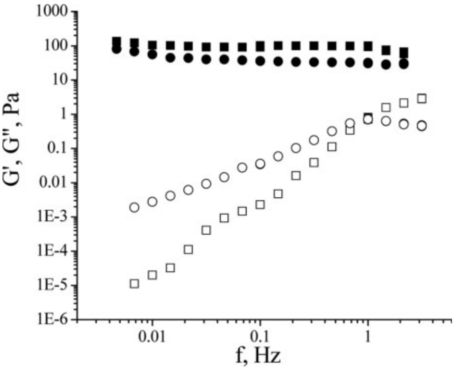

***Figure 3.***
Frequency dependencies of G' and $G''$ of aqueous solutions of HM PAAm 1.0-C12/10SA at polymer concentration of 1C* containing 1 vol.% of MP2: ■ - $G'$ in magnetic field, ● - $G''$ in magnetic field, □ - $G'$ without magnetic field, ○ - $G''$ without magnetic field.

(Figure 3). This rheological behavior is typical for the Maxwell model of viscoelastic fluid. At the same time, in the magnetic field the dispersion behaves as a gel as in the whole frequency range $G' > G''$. When the magnetic field is applied, the storage modulus increases by up to 7 orders of magnitude. Thus, under the action of the magnetic field the fluid of rather low viscosity transforms into a gel.

The reason for this behavior can be as follows. Interaction between magnetite particles under the influence of the magnetic field leads to the appearance of chain-like aggregates in the dispersion. These aggregates form a regular system of chains parallel to the direction of the magnetic field intensity. Every chain of aggregates is similar to a rod with some magnetic moment oriented along the axis of the rod. The dispersion cannot flow until the magnetite frame is not destroyed.

One can expect that the size of MP should influence the effect of the magnetic field on the rheological behavior of the dispersions. It is well known that in fields with low intensity the main contribution to the material magnetization is due to large particles. Indeed, our data show that at fixed polymer concentration the storage modulus of the dispersion based on MP2 is much higher than that of the dispersion containing smaller particles MP1 (Figure 4).

When the magnetic field is switched off, the dispersion containing MP2 returns to its initial state (Figure 5). It means that its rheological behavior becomes similar to that before the magnetic field was applied. This behavior may be due to various factors including (i) low initial viscosity and weakness of the physical gel formed under the action of magnetic filed, (ii) the small residual magnetization of MP2 (Table 1), (iii) insufficient interactions of magnetite with polymer in the solution, etc.

Thus, under the action of magnetic field the low-viscous fluid based on HM PAAm 1.0-C12/10SA at polymer concentration 1C* acquires the gel-like properties. When the magnetic field is switched off the rheological characteristics of the dispersions restore their initial values (obtained before the magnetic field was applied).

Now let us consider the MF at higher polymer concentrations (1,5C* - 2C*). They show elastic response ($G' > G''$) in wide frequency range already in the absence of magnetic field (Figure 1b). When the magnetic field is applied, we observe an increase of the elastic modulus and the transition to gel-like behavior (Figure 6). The higher the polymer concentration, the larger the values of G' (Figures 7 and 8). At fixed polymer concentration dispersions based on MP2 have the values of the

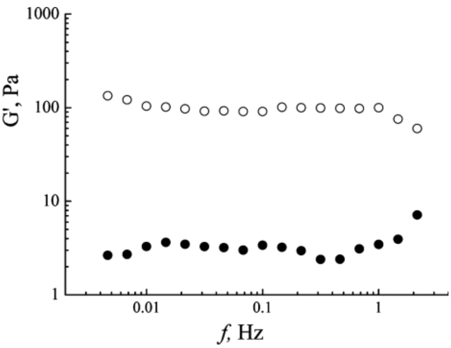

**Figure 4.**
Frequency dependencies of G′ of aqueous solutions of HM PAAm 1.0-C12/10SA at polymer concentration of 1C* containing 1 vol.% of MP in magnetic field; ● = MP1, ○ = MP2.

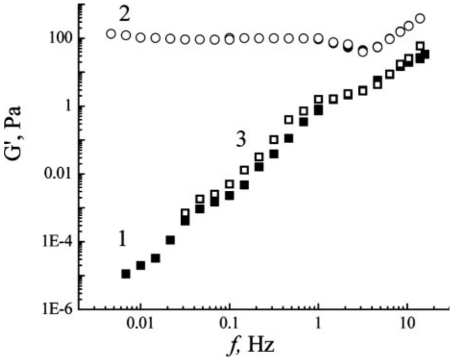

**Figure 5.**
Frequency dependencies of G′ of aqueous solutions of HM PAAm 1.0-C12/10SA at polymer concentration of 1C* containing 1 vol.% of MP2; ■ = in the absence of the field, ○ = in magnetic field, □ = after switching off the magnetic field.

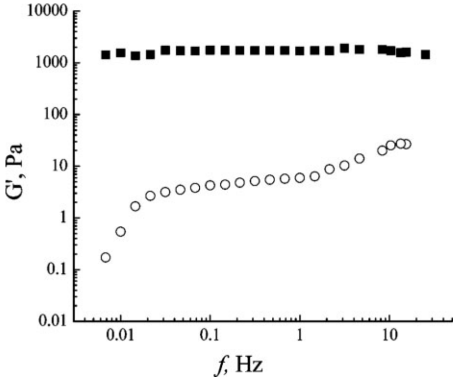

***Figure 6.***
Frequency dependencies of the storage modulus of aqueous solutions of HM PAAm 1.0-C12/10SA at polymer concentration of $2C^*$ containing 1 vol.% of MP2; ○ = without magnetic field, ■ = in magnetic field.

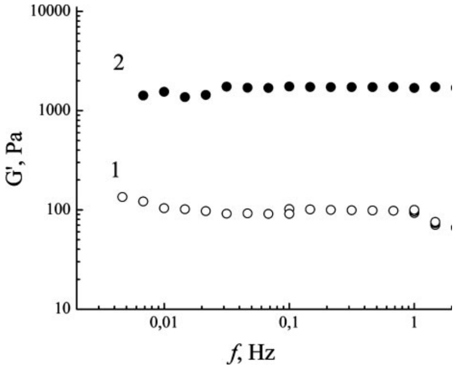

***Figure 7.***
Frequency dependencies of $G'$ of aqueous solutions of HM PAAm 1.0-C12/10SA containing 1 vol.% of MP2 in a homogeneous magnetic field at polymer concentrations $1C^*$ (○) and $2C^*$ (●).

storage moduli by two orders of magnitude larger than for those based on MP1 (cf. Figures 7 and 8). At high polymer concentration ($2C^*$) the increase of $G'$ in the magnetic field remains reversible. When the field is switched off, $G'$ drops until its initial value.

## Conclusion

The transition of low-viscous fluid into physical gel is observed under the action of magnetic field. The storage modulus of the gel was shown to increase with increasing polymer concentration and increasing size of MP. This transition is fully reversible. When the magnetic field is switched off, the storage modulus acquires its initial values.

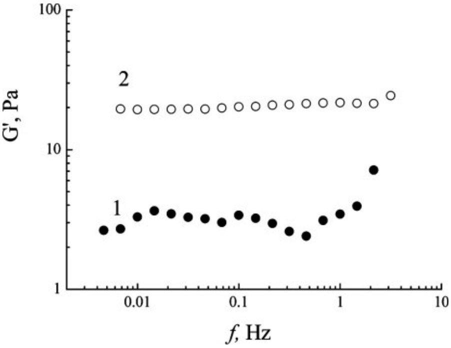

***Figure 8.***
Frequency dependencies of $G'$ of aqueous solutions of HM PAAm 1.0-C12/10SA containing 1 vol.% of magnetite MP1 in a homogeneous magnetic field at polymer concentrations $1C^*$ (●) and $2C^*$(○).

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