https://doi.org/10.15407/polymerj.48.01.015

Vadym SHUMSKY
ORCID: 0000-0003-4458-7256
Institute of Macromolecular Chemistry NAS of Ukraine
48, Kharkivske Highway, Kyiv, 02160, Ukraine
e-mail: vfshumskiy26@gmail.com
Volodymyr GRISHCHENKO
ORCID: 0000-0002-4951-936X
Institute of Macromolecular Chemistry NAS of Ukraine
48, Kharkivske Highway, Kyiv, 02160, Ukraine
e-mail: oligomer8@gmail.com
Iryna GETMANCHUK
ORCID: 0000-0002-6924-1430
Institute of Macromolecular Chemistry NAS of Ukraine
48, Kharkivske Highway, Kyiv, 02160, Ukraine
Natalia BUSKO
ORCID: 0000-0001-9831-6748
Institute of Macromolecular Chemistry NAS of Ukraine
48, Kharkivske Highway, Kyiv, 02160, Ukraine
Petro DAVYSKYBA
ORCID: 0000-0002-6735-7042
Institute of Macromolecular Chemistry NAS of Ukraine
48, Kharkivske Highway, Kyiv, 02160, Ukraine
Valeriy DAVYDENKO
ORCID: 0000-0003-0771-2679
Institute of Macromolecular Chemistry NAS of Ukraine
48, Kharkivske Highway, Kyiv, 02160, Ukraine

RHEOLOGICAL PROPERTIES OF AMPHIPHILIC FLUIDS BASED ON REACTIVE OLIGOBUTADIENE

This work investigates self-organization processes in dispersed media (matrices) that occur during shear deformation. The most relevant aspect of this self-organization is the relationship between structure and properties in dispersed systems, which largely determines the properties of future polymer composites. One of the most common dispersed media is diene oligomers (rubbers). This work examined the rheology of oligobutadienes with terminal hydroxyl (HTPB) and carboxyl (HTPB_m1) groups over a wide range of shear rates and temperatures. It was assumed that, for the studied oligobutadienes, the increase in the activation energy of viscous flow (from 33.5 to 66.4 kJ/mol) with decreasing temperature is associated with an increase in the density of the fluctuating dynamic structure with an increase in the volume content of polar OH- and COOH-group associates (i. e., non-ionic micelles) with a decrease in thermal energy kT (k is the Boltzmann constant). The results of rheological studies (for non-ionic liquids) were presented for the first time within the framework of Angel's model, which indicated that these systems are fragile, i. e., they are very promising for studying structure formation in a shear field.

***Keywords**: rheology, viscosity, shear deformation, self-organization, activation energy, Angel's model.*

Цитування: Shumsky V., Grishchenko V, Getmanchuk I., Busko N., Davyskyba P., Davydenko V. Rheological propertie of amphiphilic fluids based on reactive oligobutadien. *Полімерний журнал.* 2026. **48**, № 1. С. 15—21. https://doi.org/10.15407/polymerj.48.01.015

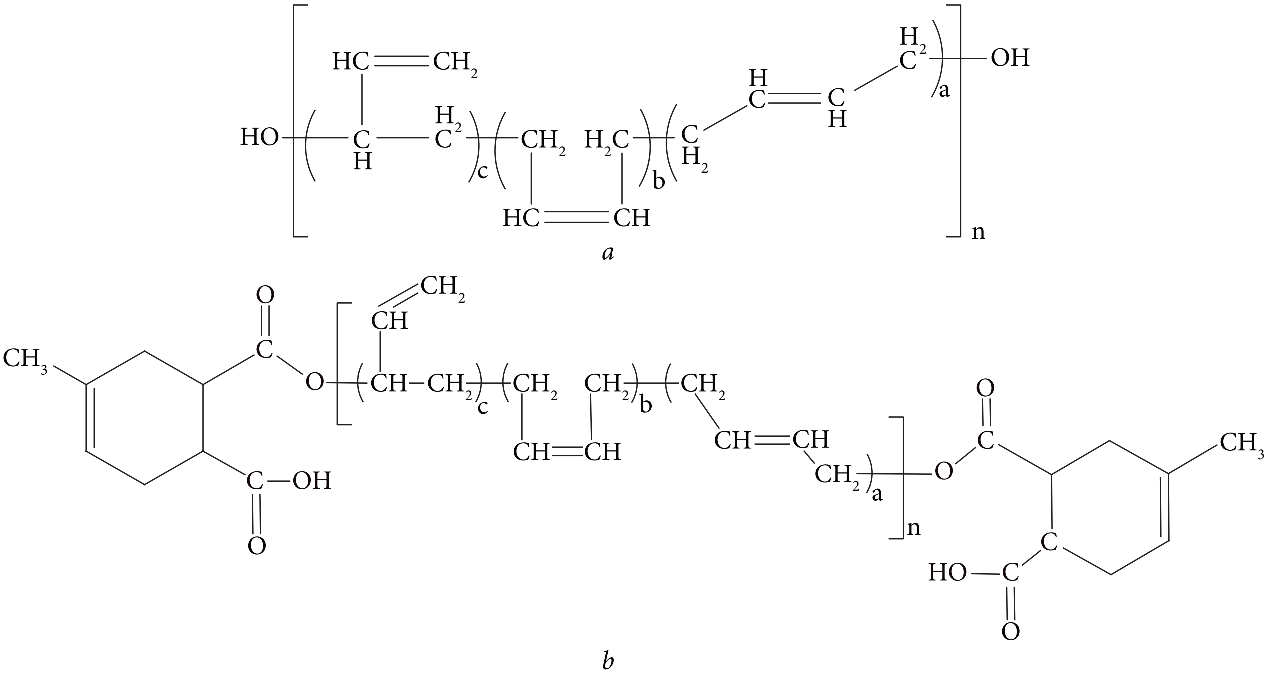
Introduction

In terms of solving the problem of creating new composite polymer materials, a relevant area of scientific research is the study of structural self-organization processes in dispersion media (matrices). It is known (see, for example, [1]) that one of the most widely used dispersion media are diene oligomers (liquid rubbers). Diene oligomers with terminal hydroxyl groups can be obtained with different molecular weights, i. e., with different contents of polar hydroxyl groups. The presence of polar groups in a non-polar hydrocarbon matrix (i. e., the amphiphilic nature of the substance molecules) leads to structure formation through the formation of non-ionic micelles during aggregation of the hydroxyl groups [2]. Aggregation occurs mainly due to hydrogen bonds. Therefore, it should be emphasized that amphiphilicity predetermines the possibility of forming various structures, i.e., it is the generator of structural self-organization [3, 4].

However, the study of the functional properties of new materials and the development of new technologies have revealed new problems that require a more detailed consideration of the complex rheological behavior of various structured systems. In general, there has been significant recent interest in developing non-classical hydrodynamic models and studying non-Newtonian fluid flows, and therefore experimental studies that reliably demonstrate the different types of flow in the same system across different shear rate ranges play a particularly important role. As G. Schramm wrote [5], "the flow curve of a sample can be called its rheological 'fingerprint,' i. e., each newly studied structured compound is unique." Therefore, a comparison of several samples is best made by comparing their flow and viscosity curves over the widest possible range of shear rates or over the range corresponding to the technological process used in their processing.

Experimental section

In this paper, the rheological properties of amphiphilic oligomeric fluids—hydroxyl-terminated oligobutadiene (HTPB, initial) obtained by radical polymerization (MW ~2800, functionality ~1.9, OH group content ~1.13%)—are presented and discussed. A sample of this oligomer modified with carboxyl groups (HTPB_m1) was then studied. Butadiene rubber with terminal carboxyl groups was stripped with isomethyltetrahydrophthalic anhydride (IMTHPA) at a molar ratio of 1:2. The reaction was monitored using IR spectroscopy by the decrease in the intensity of the C=O anhydride bands (1858 and 1777 cm^{-1}) and the appearance of



a

b

Fig. 1. Butadiene rubbers with hydroxyl (HTPB) (*a*) and carboxyl (HTPB_m1) (*b*) groups

band at 1708 and 1737 cm^{-1} due to the formation of carboxyl and ester groups, respectively. The final concentration of carboxyl groups was determined by titration.

Rheological studies were conducted in the temperature range of 5—60 °C using an Arx2000 rheometer (TA Instruments, USA) with a plane-on-plane (1 mm gap) and a cone-on-plane working unit. The experiments were primarily performed in two deformation modes:

scanning the shear rate as it increases and decreases in the range from 10^{-7} to 10^3 s^{-1}, which allows for the identification of the sample flow curve.

Results and discussion

The main experimental results are presented as flow curves in Figs 2 and 3. Here, as an example, the dependences of viscosity η and shear stress σ on the shear rate γ (Figs 2, *a* and 3, *a*) are shown, as well as the dependences of viscosity on shear stress (Figs 2, *b* and 3, *b*) for HTPB (Fig. 2) and HTPB_m1 (Fig. 3), measured at 20 °C. Similar dependences were obtained for HTPB at 5 and 20 °C, and for HTPB_m1 at 5, 30, 40, 50, and 60 °C.

The figures show that, with a decrease in shear rate from 200 to 0.1 s^{-1} and a change in temperature in the range of 5—30 °C for HTPB and from 5 to 60 °C for HTPB_m1, the viscosity of the studied compounds does not change, i. e., the fundamental equilibrium (Newtonian) values of the original and modified oligobutadienes were measured. In the low-shear-rate region, an increase in viscosity η was observed at <0.1 s^{-1}, leading to the appearance of a yield point σ_Y, indicating the formation of a fluctuation rheopex structure in HTPB and HTPB_m1. Yield points were determined from experimental data (see Figs 2 and 3) and from the Herschel-Bulkley equation (see below). The debate over whether a yield point exists or is a physically undefinable quantity has been ongoing for a long time (see, for example, [6, 7]). However, it is known that a large number of materials do not flow at low shear stresses. At the same time, over a wide range of higher shear stresses, these materials can flow and be transported like any other liquid. The boundary between these two states is understood as the "yield point." Media possessing the property described above are called viscoplastic. The yield point is one of the fundamental parameters for characterizing the properties of such materials.

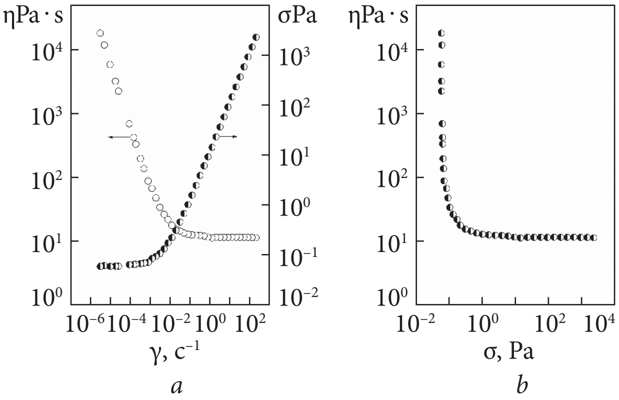


Fig. 2. Flow curves (η—γ, σ—γ (*a*) and η—σ (*b*)) of HTPB at a temperature of 20 °C

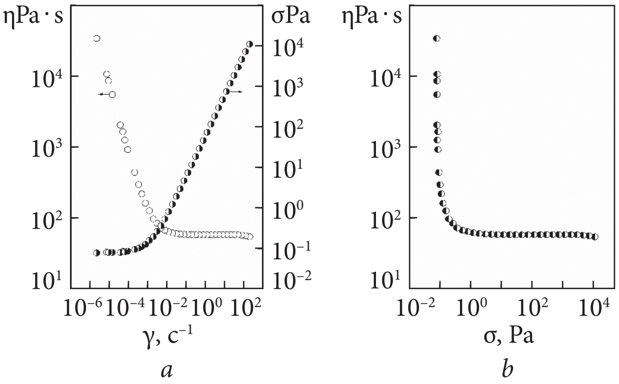


Fig. 3. Flow curves (η—γ, σ—γ (*a*) and η—σ (*b*)) of HTPB_m1 at a temperature of 20 °C

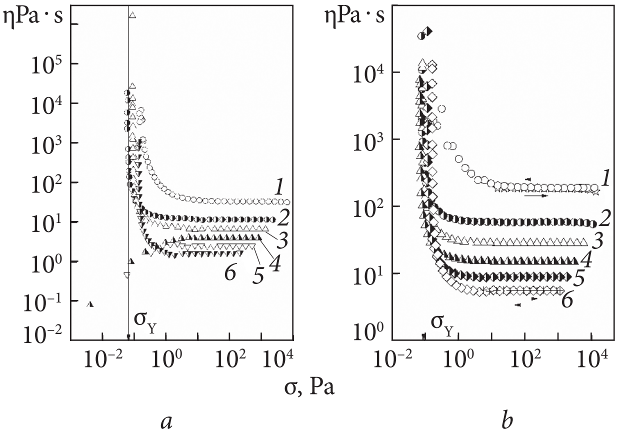


Fig. 4. Dependence of viscosity on shear stress of HTPB (*a*) and HTPB_m1 (*b*) at different temperatures (°C): 5 (*1*), 20 (*2*), 30 (*3*), 40 (*4*), 50 (*5*), and 60 (*6*). The arrows indicate the yield strength and the direction of deformation

The concept of the yield point was introduced by Bingham [8].

A large number of different rheological equations for such materials have been proposed in the

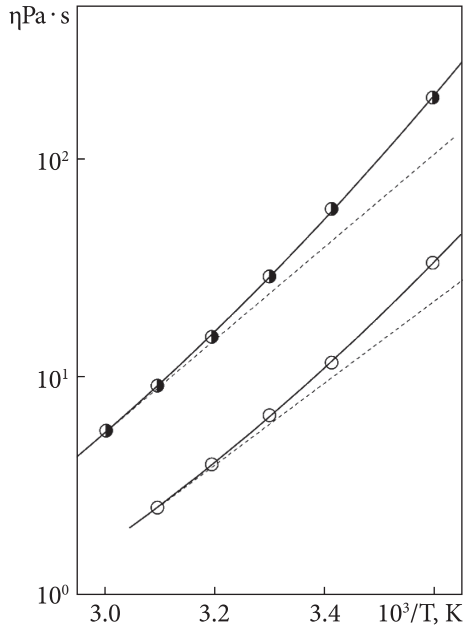


***Fig.* 5**. Temperature dependences of viscosity (in Arrhenius coordinates) of HTPB (*1*) and HTPB_m1 (*2*)

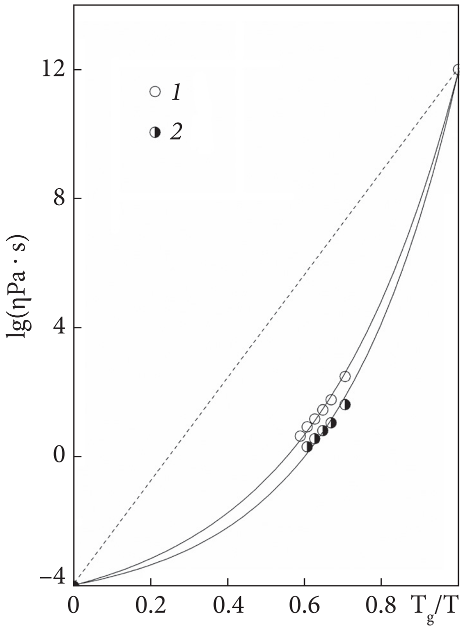


***Fig.* 6**. Temperature dependence of viscosity in the coordinates of equation (*5*) for compounds: HTPB_m1(*1*) and HTPB (*2*)

literature. Among the most popular and simple are the following equations:
the Bingham equation [8]

$$\sigma = \sigma_Y + \eta_P \dot{\gamma}, \qquad (1)$$

Casson equation [9]

$$\sigma^{1/2} = \sigma_Y^{1/2} + (\eta_P \dot{\gamma})^{1/2}, \qquad (2)$$

Herschel—Bulkley equation [10]

$$\sigma = \sigma_Y + K\dot{\gamma}^n, \qquad (3)$$

In these equations, σ_Y is the yield stress, η_P is the "plastic viscosity," K and n are experimentally determined parameters.

Plastic viscosity is a quantity distinct from the effective viscosity of a fluid. According to the standard definition, the effective viscosity of a Bingham viscoplastic medium is defined as

$$\eta = \frac{\sigma_Y + \eta_P \dot{\gamma}}{\dot{\gamma}} = \eta_P + \frac{\sigma_Y}{\dot{\gamma}}, \qquad (4)$$

Yield strength is a very important value in rheology, as it determines the formation of a structure, its strength, durability, and the characteristics of its failure. The yield strengths of HTPB $\sigma_Y = 0.0712$ Pa and HTPB_m1 $\sigma_Y = 0.106 \pm 0.024$ Pa, which are virtually independent of temperature, are considered fundamental constants of the original and modified oligobutadienes.

The dependences of viscosity on shear stress at various temperatures for the original and carboxyl-modified oligobutadienes are shown in Figures 4, *a* and 4, *b*, respectively. It should be noted that we have discovered for the first time for the studied liquid rubbers an unusual rheological effect: in contrast to the rheopex structure formation under the influence of a calm slow flow (gentle movement), in the case of the initial oligobutadiene at temperatures of 40 and 50 °C in the region of low shear rates (or stresses), a noticeable decrease in the effective (structural) viscosity with a decrease in $\dot{\gamma}$ (or σ) was recorded.

This behavior of the initial rubber is associated with a liquid-to-liquid structural transition (similar to the high-temperature transition [11]). This transition is explained [11] by the emergence of the ability to move the polymer chain as a single unit, which is ensured by an increase in free volume and the mobility of the polymer chains with increasing temperature. The physical meaning of this transition is reduced to the transformation of one amorphous state, characterized by the presence of hindered rotation mainly due to the interaction of adjacent chains, into another amorphous state in which, as the authors of the study [12] suggested, free rotation can occur. A reliable explanation of the mechanism (nature) of such an unusual effect still requires further research. Returning to Fig. 4, *b*, it should be noted that for oligobutadiene with terminal carboxyl groups, a liquid-to-liquid transition is not observed. In this case, at all temperatures studied, a liquid-to-solid transition occurs, indicating the formation of rheopex dissipative structures. We found a similar influence of terminal carboxyl groups on the structure formation of macromolecules only in the work [13].

The temperature dependences of the viscosity of the initial (1) and modified (2) oligobutadienes are shown in Fig. 5. They are satisfactorily described by the Vogel-Tammann equation [14—16]:

$$\eta = \eta_0 \exp\left(\frac{B}{T-T_0}\right) = \eta_0 \exp\left(\frac{DT_0}{T-T_0}\right), \tag{5}$$

where η_0 (Pa · s), B (K) and T_0 (K) are empirical constants (fitting parameters) for a given substance. In terms of the free volume theory, the parameter T_0 represents a certain critical temperature at which the free volume disappears. The same dependence is valid for most other liquids at lower temperatures (down to the glass transition temperature). The parameter $D = B/T_0$ of equation (5) can be used to describe the "strength" of a liquid (see below). The calculated values of the fitting parameters of this equation are given in Table 1. The temperature dependences η(1/T) of HTPB and HTPB_m1 are practically symbatical, and the main effect of modifying the initial oligobutadiene by grafting carboxyl groups to its chain consists of a noticeable increase in the viscosity and yield strength of HTPB_m1 (see Fig. 5 and Table 1).

Table 1 also presents the calculated values of the fitting parameters of the Vogel—Tammann equation: η_0, B, and T_0, η_{20}, σ_Y, T_g^η, $m_{\min}$, and m. The last three characteristics were calculated using the equations given in [4].

Table 1. **Rheological characteristics, parameters of the Vogel-Tamman equation, and brittleness of HTPB HTPB_m1**

Compound	η_{20}, Pa · s	σ_Y, mPa	η_0, mPa · s	B, K	T_0, K	T_g, K	T_g^η, K	D	$m_{\min}$	m
HTPB	11,6	71,2	3,60	1049	163	196	195	6,44	14,4	89,0
HTPB_m1	59,2	106,0	4,90	1117	174	196	208	6,42	14,3	87,8

In our case, the activation energy of viscous flow (E_T) is an effective value; it increases from 33.5 kJ/mol to 66.4 kJ/mol with decreasing temperature in the range of 5 °C—60 °C (see Table 2 below). It is related to the parameters and the relationship [17, 18]:

$$E_T = RB\left(\frac{T}{T-T_0}\right)^2, \tag{6}$$

where R is the gas constant.

It is known that the activation energy of viscous flow strongly depends on the polymer structure [4]. For example, while the activation energy of melt flow for linear polyethylene is 25 kJ/mol, for branched PE it exceeds 50 kJ/mol. Therefore, it can be assumed that in the case of oligobutadienes HTPB and HTPB_m1, the observed increase in activation energy with decreasing temperature is associated with an increase in the density of the fluctuation dynamic structure with an increase in the volume content of polar OH group associates (i. e., non-ionic micelles) with a decrease in the thermal energy kT (k is the Boltzmann constant).

We now present the rheological data within the framework of Angell's concept [19]. This concept was developed for amorphous substances. We have previously described it in detail in [2, 4]. In this article, we present Angell's model for the reactive oligobutadienes studied by us and presented in the table (Fig. 6).

It is known that the most studied characteristic of liquids is viscosity and its dependence on temperature. The equilibrium glass transition temperature is usually defined as the temperature at which the viscosity is 10^{12} Pa · s. Another generally accepted result of observation is that at infinitely high temperatures, the limiting viscosity $\eta_0 \approx 10^{-4}$ Pa · s.

Consequently, in the temperature range between $T \to \infty$ and T_g, the viscosity changes by 16 orders of magnitude. These data were used by Angell to clas-

Table 2. **Activation energy of the E_T flow of HTPB and HTPB_m1**

Compound	E_5, kJ/mol	E_{30}, kJ/mol	E_{40}, kJ/mol	E_{50}, kJ/mol	E_{60}, kJ/mol
HTPB	50,0	40,9	38,0	36,0	33,5
HTPB_m1	66,4	51,2	47,1	43,6	40,7

sify liquids by constructing a phase diagram. The diagram shows a semi-logarithmic dependence of viscosity on temperature, normalized by T_g, i. e., log η_0 — T_g/T. A diagram for the studied oligobutadiene liquids is shown in Fig. 6. Here, the straight dotted line represents the interface between two classes of liquids: strong ("strong" according to [19]) and fragile ("fragile" according to [19]).

According to Angell's concept, the systems studied are generally brittle; that is, they can self-organize and readily form rheopex dissipative structures under the influence of a shear field. These structures remain stable over long periods of time with a continuous input of dissipative energy. However, recent studies [20] have shown that such dissipative structures, when formed in sufficient quantities, form ensembles and, through the cooperative interaction of these ensembles, can subsequently create sufficiently strong and stable structures that also exhibit flexibility. The reactive liquid rubber samples we examined showed strong potential as the foundation for new soft materials.

Authors Contributions

This article was written with the contribution of all authors. All authors approved the final version of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1. *Shumsky V.F., Boiko V.P., Getmanchuk I.P., Grishchenko V.K., Nistratov A.V., Novakov I.A.* Viscosity of oligoisoprenes obtained by radical polymerization. Kautchuk und Gummi, 2012, **6**: 47—50.
2. *Shumsky V.F., Getmanchuk I.P., Boiko V.P., Grishchenko V.K.* Rheological properties of oligoisoprene liquids. Presentation in the framework of the Angell's concept. Polimernyi Zhurnal, 2023, **45**, 2: 97—102. https://doi.org/10.15407/polymerj.45.02.097
3. *Shumskii V. F., Shevchenko V. V., Gumennaya M. A., Getmanchuk I. P., Stryutskii A. V., Klimenko N. S., Davidenko V. V., Ignatova T. D., Syrovets A. P., Vorontsova L.A.* Specific features of the rheological behavior of a protic oligomeric ionicliquid of cationic type with basic sites of two types in the region of the of the solid — liquid transition. Colloid J. 2019, **81**, 6: 804—816. https://doi.org/10.1134/S1061933X19050132
4. *Shumskii V.F., Getmanchuk I.P., Shevchenko V.V., Gumennaya M. A., Stryutskii A. V., Davidenko V. V., Kravchenko V.V.* Influence of shear deformation on the formation of dynamic structure in protic ionic liquids. Representation of the temperature dependence of viscosity within the framework of Angell's fragility concept. J. Mol. Liquids, 2024, **401**, 124633, https://doi.org/10.1016/j.molliq.2024.124633.
5. *Schramm G. A.* Practical Approach to Rheology and Rheometry. Karlsruhe, Gebruder YAAKE. 1994, 311 p.
6. *De Kee D., Chan Man Fong C.F.* Letter to the Editor: A true yield stress? J. Rheol. 1993, **37**, 4: 775—776. https://doi.org/10.1122/1.550394
7. *Spaans R.D., Williams M.C.* Letter to the Editor: At last, a true liquid-phase yield stress. J. Rheol. 1995, **39**, 1: 241—246. https://doi.org/10.1122/1.550684
8. *Bingham E.C.* Bull. US Bur. Stand. 1916, **16**, P. 39.
9. *Casson N.* Rheology of Disperse Systems, Pergamon, Oxford. 1959.
10. *Hershel W.H., Bulkley R.* Proc. Amer. Assoc. Test. Materials. 1926, **26,** P. 621; Kolloid Z. 1926, **39**, P. 291. https://doi.org/10.1007/BF01432034
11. *Boyer R.F.* Transitions and Relaxations in Polymers (edited by R.F.Boyer) Intersci. Publish. Divis. John Wiley & Sons, Inc., 1966, P. 305.
12. *Krimm S., Tobolsky V.* X-ray pattern of polystyrene as a function of temperature J. Polymer Sci., 1951, **6**, 5: 667—668. https://doi.org/10.1002/pol.1951.120060518
13. *Kobayashi T., Ikeda S., Osaki K.* Study on pigment dispersing resins — The effect of resins terminated with carboxyl groups. J. Rheol. 1993, **37**, 3: 549— 556. https://doi.org/10.1122/1.550410
14. *Vogel H.* The temperature dependence law of the viscosity of fluids. Phis. Z. 1921, **22**, 645—646.
15. *Fulcher G.S.* Analysis of recent measurements of the viscosity of glasses J. Am. Ceram. Soc. 1925, **8**, 339—355. https://doi.org/10.1111/j.1151-2916.1925.tb16731.x
16. *Tammann G.* Der Glaszustand . Leipzig: L.Voss Verlag. 1933.
17. *Berry G.C., Fox T G.* The viscosity of polymers and their concentrated solutions. Adv. Polym. Sci. 1968, **5**, 3: 261—357. https://doi.org/10.1007/BFb0050985

18. *Miller A.A.* Some molecular properties of vinyl polymers. Macromol. 1969, **2**, 2: 355—358. https://doi.org/10.1021/ma60010a007
19. *Angell C. A.* Relaxation in liquid, polymers and plastic crystals — strong/ fragile patterns and problems. Journal of Non-Crystalline Solids. 1991, **131**: 13—31. https://doi.org/10.1016/0022-3093(91)90266-9
20. Nanotekhnolohii u farmatsii ta medytsyni (za red. O.F.Piminova). Vyd. “Fakt”, Kharkiv, Ukraina, 2014, Tom 1, 672 s.

Received 30.10.2025
Accepted 05.01.2026
Published 31.03.2026

Вадим Шумський
ORCID: 0000-0003-4458-7256
Інститут хімії високомолекулярних сполук НАН України
48, Харківське шосе, Київ, 02155, Україна
e-mail: vfshumskiy26@gmail.com
Володимир Грищенко
ORCID: 0000-0002-4951-936X
Інститут хімії високомолекулярних сполук НАН України
48, Харківське шосе, Київ, 02155, Україна
e-mail: oligomer8@gmail.com
Ірина Гетьманчук
ORCID: 0000-0002-6924-1430
Інститут хімії високомолекулярних сполук НАН України
48, Харківське шосе, Київ, 02155, Україна
Наталія Бусько
ORCID: 0000-0001-9831-6748
Інститут хімії високомолекулярних сполук НАН України
48, Харківське шосе, Київ, 02155, Україна
Петро Давискиба
ORCID: 0000-0002-6735-7042
Інститут хімії високомолекулярних сполук НАН України
48, Харківське шосе, Київ, 02155, Україна
Валерій Давиденко
ORCID: 0000-0003-0771-2679
Інститут хімії високомолекулярних сполук НАН України
48, Харківське шосе, Київ, 02155, Україна

РЕОЛОГІЧНІ ВЛАСТИВОСТІ АМФІФІЛЬНИХ РІДИН НА ОСНОВІ РЕАКЦІЙНОЗДАТНОГО ОЛІГОБУТАДІЄНУ

Робота присвячена дослідженню процесів самоорганізації в дисперсійних середовищах (матрицях), що відбуваються при їх зсувному деформуванні. Найбільш актуальним аспектом такої самоорганізації є взаємозв’язок структури та властивостей у дисперсних системах, що багато в чому визначає властивості майбутніх полімерних композитів. Одним із найпопулярніших дисперсійних середовищ є дієнові олігомери (каучуки). У цій роботі було досліджено реологію олігобутадієнів з кінцевими гідроксильними (HTPB) та карбоксильними (HTPB_m1) групами в широкому діапазоні швидкостей зсуву та температури. Припустили, що у разі досліджених олігобутадієнів збільшення енергії активації в’язкої течії (від 33,5 до 66,4 кДж/моль) при зменшенні температури пов’язане зі збільшенням щільності флуктуаційної динамічної структури зі зростанням об’ємного вмісту асоціатів полярних OH- і COOH-груп (т. е. Больцмана). Результати реологічних досліджень вперше (для неіонних рідин) було представлено в рамках концепції Анжела, звідки випливало, що ці системи належать до крихких (fragile), тобто вони дуже перспективні щодо дослідження структуроутворення в зсувному полі.

Ключові слова: *реологія, в’язкість, деформація зсуву, самоорганізація, енергія активації, модель Анжела.*