

Analysis of Phase Transitions of Thermoresponsive Polymer Based on N-Vinylcaprolactam and 2-Hydroxyethyl Acrylate in Solutions from the Information Theory Point of View

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Abstract

A new method for analyzing phase transitions in solutions of thermoresponsive polymers is proposed, based on determining the amount of information contained in the curve describing the phase transition. The method is based on the use of an analogy with the Nyquist-Shannon-Kotelnikov theorem, which allows us to bring the analysis of a continuous function to the analysis of its values at discrete points, as well as the results of studies of slowly changing signals from the point of view of modern information theory. This analogy allows us to determine the minimum number of parameters that describe the phase transition. The proposed method was tested using the example of phase transitions in solutions of thermoresponsive copolymers of N-vinylcaprolactam with 2-hydroxyethyl acrylate of various compositions. The effectiveness of this method has been demonstrated; in particular, it has been shown that the number of parameters that describe the phase transition in this case does not exceed four. The possibilities of using the proposed method for constructing a classification of phase transitions in solutions of stimulus-sensitive polymers are discussed.

1. Introduction

The ability to undergo phase transitions is one of the main properties of stimulus-sensitive polymers and hydrogels based on them [1–5]. An important variety of them is thermoresponsive polymers, in which a phase transition occurs with relatively small temperature variations, leading to a shift in the hydrophobic-hydrophilic balance [6–10].

Over the past few decades, the current literature has accumulated a very large amount of information reflecting the properties of thermoresponsive

polymers of various varieties [3, 11], as well as their complexes with high- and low-molecular substances [12, 13]. It is known [14, 15] that the formation of complexes between polymers of different natures with low- and high-molecular substances in itself can initiate phase transitions, i.e. the formation of a complex of this type, but formed with the participation of a thermoresponsive polymer, often leads to very nontrivial effects, also reflected in the literature [16, 17].

Generalizing such a significant array of experimental results reflecting the behavior of thermoresponsive polymers and complexes formed with their participation is a very non-trivial task, requiring, among other things, the development of an appropriate methodology.

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It is advisable to build such a methodology based on the semi-phenomenological theory of phase transitions. Indeed, theoretical models currently constructed [18, 19], as well as computer simulations based on them, most often lead to results that are as difficult to interpret and develop simple classification features as experimental data.

As emphasized in [20], de facto we are talking about a very specific problem of a methodological nature: modern computing technologies make it possible to simulate processes of almost any degree of complexity, but as the complexity of programs increases, the connection between the control parameters embedded in the program and the nature of the results obtained becomes increasingly more difficult to comprehend.

Therefore, it is advisable to pose the question differently. There is a certain body of experimental data, for example, reflecting the nature of phase transitions in thermoresponsive polymers and complexes based on them. Each of the curves obtained in the experiment carries a de facto limited amount of information, which follows, among other things, from general physical considerations. Indeed, the change in the state of macromolecules in solution (or the state of a cross-linked network) with a temperature change is described by a smooth curve, since there is a scatter in the characteristics of macromolecules according to any of the control parameters. Otherwise, the curves describing the phase transition of the type under consideration are slowly changing in the sense taught by information theory [21]. The amount of information de facto contained in such curves is limited, which correlates with the well-known Nyquist-Shannon-Kotelnikov theorem [22].

Specifically, this theorem states that if a function describing a certain process (for example, a signal) has a limited radio frequency spectrum, then, regardless of the nature of the process under study, instead of a continuous function, its values at discrete points (samples) can be considered. This allows us to raise the question of measuring the amount of information carried by a continuous curve describing a particular process, including a phase transition.

It is this circumstance that makes us consider semi-phenomenological theories of phase transitions as a basic tool for systematizing the accumulated volume of experimental data.

Indeed, the curves describing phase transitions for different polymers may have different shapes, but the amount of information they contain is limited. Consequently, to solve the problem outlined above, it is necessary to develop a technique that will allow, from

a uniform point of view, to determine the minimum amount of information that allows a comprehensive description of any curves describing phase transitions experienced by thermoresponsive polymers.

The goal of this work is to develop a methodology that allows us to minimize the amount of information sufficient for a comprehensive description of any phase transitions experienced by thermoresponsive polymers and allows us to further proceed to the development of classification characteristics on this basis.

2. Materials

N-vinylcaprolactam (NVCL) with a main product content of 98% produced by Sigma-Aldrich Chemie GmbH (Germany) was used without additional purification, $T_{\text{boil.}} = 128\text{ }^{\circ}\text{C}/21\text{ mmHg}$, $n_D^{20} = 1.0500$.

2-hydroxyethyl acrylate (HEA) from Sigma-Aldrich Co. (USA) with a main product content of 96% was further purified by passing through a column filled with aluminum oxide (Al_2O_3), Bp. = $90\text{--}92\text{ }^{\circ}\text{C}/12\text{ mmHg}$, $n_D^{20} = 1.4500$.

Ethanol (absolute with boiling point = $78\text{ }^{\circ}\text{C}/760\text{ mm Hg}$, $n_D^{20} = 1.3612\text{--}1.3618$) produced by Sigma-Aldrich Co. (USA) were used without further purification. Diethyl ether (absolute boiling point = $34.6\text{ }^{\circ}\text{C}/760\text{ mm Hg}$, $n_D^{20} = 1.3530$, Sigma-Aldrich Co., USA) was used without additional purification.

N-vinylcaprolactam (NVCL) and 2-hydroxyethyl acrylate (HEA) copolymers (NVCL-HEA copolymers) were obtained by γ -radiation copolymerization in ethanol solutions by using MRX-g-25 M set-up (Russia) equipped with ^{60}Co source as describe in [23].

The resulting copolymers were purified by reprecipitation from ethanol into diethyl ether, followed by drying in a vacuum oven.

The composition of the NVCL-HEA copolymers was determined by ^1H NMR spectroscopy in deuterated dimethyl sulfoxide (DMSO-d_6) using a Bruker Avance III 400 MHz NMR spectrometer (USA) based on the ratio of intensities corresponding to peaks $\delta = 4.0\text{ ppm}$ (signals of $-\text{CH}_2-$ groups 2-hydroxyethyl acrylate (HEA) and $\delta = 3.1\text{ ppm}$ (signals of $-\text{CH}_2-$ groups in the lactam ring NVCL).

The weight-average molecular weights and molecular weight characteristics of the PVCL homopolymer and copolymers NVCL-GEA and NVCL-AA of various compositions were determined using gel permeation chromatography using a Waters ALC 201 GPC device, (Great Britain). Tetrahydrofuran was used as an eluent (mobile phase) at a flow rate of 1.0 ml/min . Molecular masses were calibrated according to polystyrene standards.

IR spectra of the original polymer samples and their interpolymer complexes (IPC) were recorded on a Perkin-Elmer FTIR Spectrum Two spectrophotometer (UK) in the range of 4000–800 cm^{-1} . Samples were prepared in the form of KBr tablets.

Figure 1 shows the ^1H NMR spectra of the obtained copolymers of various compositions. It can be seen that integration and taking into account the ratio of the intensity of the signals observed in the region of chemical shifts at 4.0 ppm characteristic of the methylene group of HEA and the signal in the region of 3.1 ppm related to the protons of $-\text{CH}_2-$ groups in the lactam ring NVCL, allows us to determine the composition of the copolymers and calculate the copolymerization constants (r_1 and r_2) for monomers during copolymerization. The composition of the initial monomer mixture (IMC, Feed), the compositions of the copolymers, and their molecular weight characteristics are presented in Table 1.

IR spectra were also recorded for the synthesized copolymers based on NVCL and HEA. Figure 2 shows the IR spectra of NVCL-HEA copolymers obtained with different IMC compositions. The spectra of the copolymers contain intense stretching vibrations of the carbonyl group, characteristic of NVCL and HEA units at 1612 cm^{-1} and 1720 cm^{-1} , respectively. The presence of the hydroxyethyl ether group of HEA is confirmed by the presence of a series of double peaks of C–O and C–O–C stretching vibrations in the region of 1200–1160 cm^{-1} and 1080–1050 cm^{-1} , respectively. The intensity, shape and position of the peaks of the C=O and C–O–C stretching vibrations depend on the composition of the IMC; this is apparently due to the interaction between the NVCL and HEA units. It is obvious that a decrease in the

NVCL content in the IMC leads to an increase in the relative intensity of the vibration peaks of the hydroxyethyl ether group of HEA. At the same time, the spectrum shows shifts in the absorption bands of the carbonyl group from 1633 cm^{-1} to 1612 cm^{-1} and the amide group from 1508 cm^{-1} to 1480 cm^{-1} NVCL in the copolymer.

Table 1. The ratio of IMC compositions and copolymer compositions, molecular weight characteristics of thermo-sensitive copolymers NVCL-HEA

#	Composition of the IMC [NVCL]: [HEA], mol.%	Copolymer composition ¹ [NVCL]: [HEA], mol.%	M_w^2 (kDa)	M_n^2 (kDa)	M_w/M_n^2
1	100	100	30	25.5	1.18
2	90:10	52:48	121.2	73.4	1.65
3	80:20	50:50	147.5	91.6	1.61
4	70:30	45:55	179.4	106.5	1.68
5	60:40	42:58	202.7	114.8	1.77
6	50:50	32:68	264.1	138.4	1.91

¹ Determined by ^1H NMR spectroscopy

² Determined by GPC method

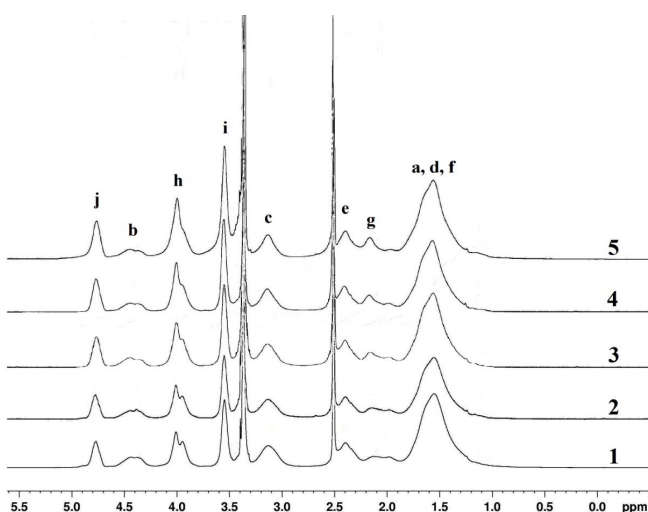


Fig. 1. ^1H NMR spectra of NVCL-HEA copolymers in DMSO-d_6 ; composition of copolymers [NVCL]:[HEA], mol. %: 52:48 (1); 50:50 (2); 45:55 (3); 42:58 (4); 32:68 (5).

The studied thermoresponsive copolymers (SPLs) of N-vinylcaprolactam (NVCL) with 2-hydroxyethyl acrylate (HEA) of various compositions were obtained by radical copolymerization according to the method of [23] using commercially available starting reagents without additional purification.

To determine the chemical composition of the resulting SPLs, NMR(H1) spectroscopy was used; DMSO-d_6 was used as a solvent.

This copolymer was chosen based on the characteristics of the phase transition, the nature of which (from the point of view of applying information theory methods) differs significantly from that studied in [24, 25]. As will be clear from what follows, these features make it possible to reveal the essence of the proposed methodology using a single example.

Among all the obtained polymers, a sample was selected that corresponds to the most asymmetric phase portrait (this method is discussed in Section 3). We emphasize that the phase portraits studied in [24, 25] had a pronounced symmetry relative to the inflection point of the curve of the dependence of optical density on temperature. For comparison, as well as to prove the applicability of the proposed methodology in the general case, a sample was selected whose behavior deviates as much as possible (in terms of the nature of the phase portrait) from those studied in [24, 25].

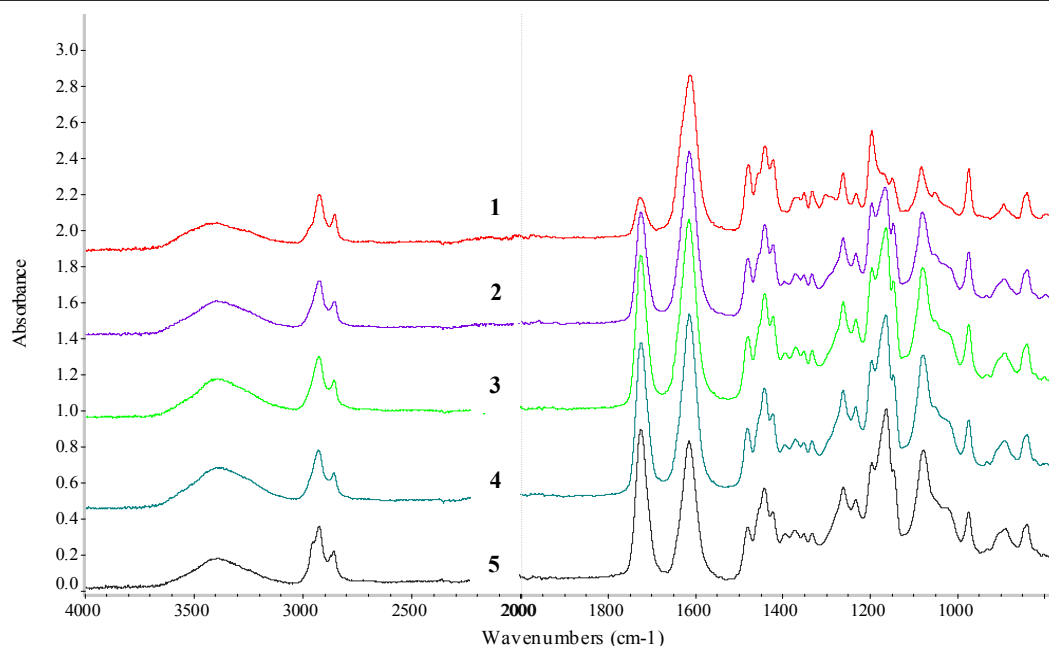


Fig. 2. IR spectra of NVCL-HEA copolymers; IMC composition [NVCL]:[HEA], mol.:%90:10 (1); 80:20 (2); 70:30 (3); 60:40 (4); 50:50 (5).

3. Methods

The optical density of aqueous solutions of copolymers was studied by turbidimetry at a wavelength of 400 nm on a spectrophotometer using a thermostatic cell using a thermionic cuvette controller “CPS-240A Shimadzu” (Japan).

We emphasize that the turbidity of the solution under study in this work is measured in relative units. In this case, as a measure reflecting turbidity, it is permissible to use the signal amplitude directly recorded by the measuring device. A similar approach was previously used in [26].

The main method of processing experimental data used in this work is the method of phase portraits, proposed in [27] and further applied in [24, 25] to establish the patterns of behavior of polymer solutions undergoing a phase transition. As shown in the cited works, as well as in [28–31], this method allows one to establish the features of phase transitions in polymer solutions, as well as determine the values of critical parameters with increased accuracy. Note that the problem of finding criteria that provide classification of a significant amount of data on phase transitions in solutions of the type under study was also solved in [31]. However, in the cited work, a different approach was used, based on the selection of segments of phase portraits that obey simple differential equations. In this work, on the contrary, we use an approach focused on determining the amount of information that an experimental curve can carry.

4. Experimental part

Figure 3 shows the dependence of the optical density (turbidity) of aqueous solutions of the NVCL-GEA copolymer of various concentrations on temperature. The copolymer composition and its concentration related to the different curves are indicated in the figure legend. The dots correspond to the experimental results, the solid lines are constructed using the semi-phenomenological theory discussed in the next section.

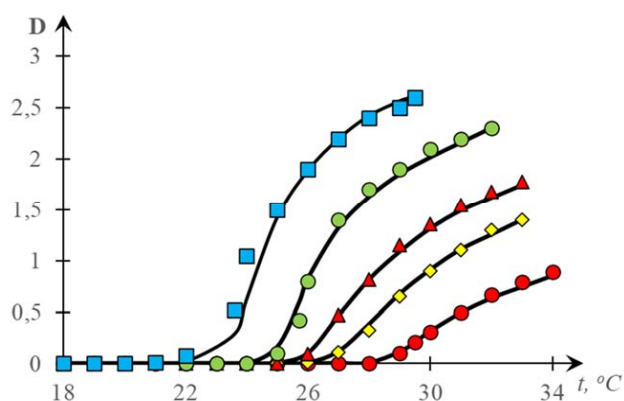


Fig. 3. Temperature dependence of the optical density (turbidity) of aqueous solutions of the NVCL-HEA copolymer of various concentrations; composition of copolymer [NVCL]:[HEA] = 42.5:57.5 mol.%; $C_{\text{copolymer}}$ = 0.5 (1); 1.0 (2); 2.0 (3); 5.0 (4); 10.0 mg/ml (5); dots – experimental data, solid lines – the result of applying semi-phenomenological theory.

It can be seen that the behavior of the copolymer under study with increasing temperature can be interpreted as a phase transition. Indeed, the turbidity of a solution varies from one limiting value to another in a relatively narrow (less than 100C) temperature range. It can also be seen that the phase transition temperature noticeably depends on the concentration of the polymer in the solution. This behavior of the copolymer under study is, on the one hand, quite typical [24, 25]. On the other hand, the nature of the phase transition under consideration, as will be clear from what follows, has well-defined features that make it possible to use it as an example for constructing a general methodology for analyzing phase transitions in solutions of thermoresponsive polymers from the point of view of information theory.

5. Results and discussion

In Fig. 4 (a-e) shows phase portraits of the curves shown in Fig. 1. Phase portraits were constructed according to the above method [25]. In accordance with the phase portrait method, the graphs presented in Fig. 4 represent the dependence of $Q = d_D/d_T$ on D . This dependence in certain cases allows us to empirically obtain a differential equation describing the dependence of the optical density of the solution on temperature. In [24, 25] was shown that there are specific examples of phase transitions that are described by a Ricatti-type differential equation, which gives a solution in the form of a logistic curve. This creates the prerequisites for trying

to determine the amount of information that the phase portrait carries.

It can be seen that, unlike the phase portraits obtained in the cited works, these phase portraits are not symmetrical, and therefore, it is impossible to use their parabolic approximation.

However, the range of change of the current variable for any phase portrait corresponding to a phase transition is certainly finite. Specifically, the variable D (turbidity variable) varies from zero to D_{max} (the value corresponding to the situation when all the macromolecules present in the solution have changed their state).

Consequently, to approximate the phase portrait, the Fourier series expansion with a period (or half-period) specified by the initial and final values of D is applicable. Considering that, due to the specifics of the problem under consideration, the condition is satisfied

$$Q|_{D=0} = 0$$

it is convenient to assume that the range of change of the current variable of the phase portrait $D \in [0, D_{max}]$ corresponds exactly to the half-cycle.

In this case, a formally antisymmetric function can be considered; therefore, only sinusoidal components remain in the Fourier series expansion. We have

$$Q(D) = \sum_{k=1}^{k=\infty} b_k \sin\left(\frac{2\pi}{2D_{max}} kD\right)$$

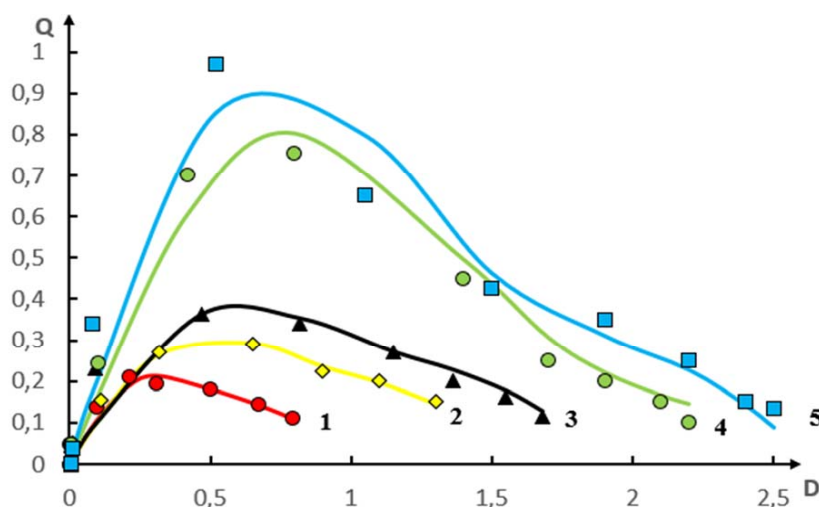


Fig. 4. Phase portraits of the curves shown in Fig. 2, curves 1 – 5 correspond to figures a) – e); dots are the result of applying numerical differentiation to the experimental curves, solid lines are the result of applying approximation through a Fourier series with a finite number of terms.

In this formula, the period of the function under consideration is formally equal to $2D_{max}$, which is emphasized by the cancelable factor 2 in the expression under the sine sign.

Further, from the most general considerations of information theory [21], it follows that if the function under consideration has a limited derivative over the entire range of values of the current variable, then its spectrum is obviously limited. Let us recall that from the well-known Nyquist-Shannon-Kotelnikov theorem it follows that instead of a continuous signal having a limited spectrum, it is permissible to consider its values on a set of discrete points. Otherwise, a continuous function with a limited spectrum is exhaustively described in terms of its values at a certain set of discrete points. In relation to the problem under consideration, this means that a process that obviously has a limited derivative can be exhaustively described through series (2) with a finite number of terms.

Solid lines in Fig. 2 shows the result of approximation of phase portraits obtained by the method of numerical differentiation of experimentally obtained curves using series (2) containing three terms. The specific values of the parameters used are given in Table 2.

Numerical values of the parameters of series (2), used in constructing approximations of phase portraits, Fig. 2.

Table 2. Used parameters

n	D_{max}	b1	b2	b3
1	1.01	0.205	0.04	0.025
2	1.61	0.295	0.06	0.037
3	1.93	0.36	0.08	0.045
4	2.87	0.57	0.32	0.1
5	2.65	0.72	0.32	0.14

It can be seen that the nature of the phase portrait under consideration really allows it to be described through a limited set of parameters with acceptable accuracy. Consequently, the curves under consideration are indeed described through a limited set of parameters.

Evidence of the adequacy of the method used is presented in Fig. 1. Namely, by numerical integration (the operation inverse to numerical differentiation) the dependencies were found using approximations of phase portraits using the parameters presented in Table 1. These dependencies are shown in Fig. 1 with solid lines. It can be seen that the calculated and ex-

perimental data coincide with acceptable accuracy, i.e. the actual number of parameters that describe experimental data does not exceed four. Note also that for the phase transitions studied in [24, 25], this number did not exceed two.

6. Conclusions

Thus, the method of phase portraits, as well as the analogy with the Nyquist-Shannon-Kotelnikov theorem, allows us to propose a relatively simple method for determining the minimum number of parameters characterizing the phase transition in solutions of thermoresponsive polymers. The example of a solution of a thermoresponsive copolymer of N-vinylcaprolactam with 2-hydroxyethyl acrylate considered in the work shows that this method makes it possible to obtain approximations of curves describing the phase transition, including in cases where the phase portrait is quite complex, in particular, different from parabolic. The results obtained are consistent with the conclusions made in studies of slowly changing signals, also based on the use of the above theorem. The number of parameters that comprehensively characterize the phase transition in solutions of a thermoresponsive polymer must be relatively small due to the specifics of the system under consideration. In particular, in the example considered in this work, it does not exceed four. This result allows us to raise the question of constructing a semi-phenomenological classification of phase transitions of the type under consideration based on calculating the minimum number of parameters that comprehensively describe such a transition in various specific cases.

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