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Use of Reversed Gas Chromatography in the Investigation of Polymeric Compounds

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The principal aspects of the use of gas chromatography for investigating polymers when they are employed as a stationary phase (the reversed gas chromatographic method) are considered: the identification of polymers, the determination of their molecular weights, the study of the thermodynamics of the dissolution of low-molecular-weight substances in polymers, the determination of the temperatures of the phase transformations, degrees of crystallinity, kinetics of crystallisation processes, and the chemical changes taking place in the polymers.
The theoretical principles of the use of reversed gas chromatography and the peculiarities of the gas-chromatographic behaviour of polymers determined by the structure and their phase and physical states are discussed. 67 References.

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I. INTRODUCTION

The classical version of the gas-chromatographic method cannot be used directly for investigating involatile high-molecular-weight compounds. Destructive gas chromatography is an indirect method, since it is based upon the correlation between the characteristics of the polymeric system being studied and the spectrum of products for its pyrolysis or from other chemical changes.

Another, qualitatively different, approach to the investigation of high-molecular-weight compounds is possible—the use of reversed gas chromatography (RGC). In RGC the system being studied is, unlike the classical version, the stationary phase, on which known volatile compounds (standards) are separated. RGC is based on the use of the direct interaction of the standard chromatographable compounds with the polymeric system being studied and the establishment of a definite connection between the chromatographic characteristics of the standard compounds and the composition, structure, and other properties of the polymeric system used as the stationary phase. Therefore the RGC method can be regarded as a direct method of investigation of high-molecular-weight compounds.

Martin[1] was the first to report the value of gas–liquid chromatography (GLC) in the study of the thermodynamics of the interaction of volatile substances with an involatile phase. The terminology "reversed gas chromatography" was proposed in 1966.[2,3]

Initially RGC was regarded as a method of solving separate, rather general problems: identification[4,5], determination of phase transformations[6,7], study of kinetics[8,9], etc. The wider concept of RGC as a physicochemical and analytical method of investigation of involatile systems was proposed by one of us[2,3].

The possibility in principle of using RGC as an independent analytical method for identification was first stated by Zhukovitskii and Turkel'taub[4]: "In individual instances the test substance can be used as a stationary phase, with the aim of identifying the components and finding the presence of impurities of a definite nature. For example, the presence of polar impurities in a non-polar solvent has a marked effect on the retention time for polar impurities".

The RGC method can be used for investigating both liquid and solid substances. In the investigation of polymers as stationary phases in each specific instance preliminary consideration must be given to the mechanism of the chromatographic process (absorption, adsorption, mixed), which is determined by the possibility of using recently developed theories of gas–liquid or gas–adsorption chromatography to obtain the physicochemical characteristics of polymeric specimens.

Owing to the widespread use of polymers in the practice of modern gas chromatography as liquid stationary phases (silicone oils, polyglycols, polyethers, rubber) and as solid adsorbents and carriers (porapaks of various grades, polyurethanes, polyalkenes, etc.) much material has accumulated on the retention volumes of various volatile compounds on polymeric phases. An analysis of these results can give valuable information in the study of many specific problems. The aim of the present review, however, is to find the main regions and prospective uses of RGC in the investigation of polymeric compounds.

II. IDENTIFICATION OF POLYMERS

Experimental verification of the applicability of reversed chromatography for identification purposes showed that this method permits group identification of the compounds used as stationary phase[5]. As an example, Fig. 1 gives the relative retention times for substances of different polarities (methanol, heptane, toluene) in a triangular coordinate system, when normal alkanes, aliphatic alcohols, and acids are used as stationary liquid phase. It was found that each of these homologous series is characterised by a sharply defined range of values of the retention times of standard compounds. We note that this method makes it possible even to distinguish some isomeric compounds. Thus the spectra of standard

volatile compounds are different for 1,3-butylene glycol and 1,4-butylene glycol, and also for primary and secondary octyl alcohols. The results given show the rather high sensitivity of the method of reversed chromatography. Similar results can also be obtained for polymeric systems.

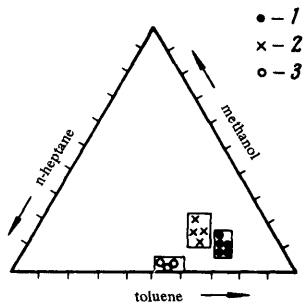


Figure 1. Diagram for group identification by three standard components: *1*) aliphatic acids; *2*) normal aliphatic alcohols; *3*) n-alkanes.

The large body of information that has accumulated in gas chromatography on the use of polymers as stationary liquid phases for separating mixtures of volatile compounds (for example, see McReynolds [10] and Lewis [11]) suggests that polymers can also be identified by RGC. Thus according to Devyatykh and coworkers [12] the retention volume for phosphine on a column with silicone oil 702 is 1.75 cm^3, with silicone oil VKZh-94 B it is 1.58 cm^3, and with silicone oil PFMS-4 it is 2.52 cm^3. Another example is of two polymeric compounds of the same type—poly(propylene glycol) with $\bar{M}_n$ = 1760 and poly(ethylene glycol) with $\bar{M}_n$ = 1540, which are characterised by markedly different retention values [10], which allows the RGC method to be used for their identification (see Table 1). RGC results for the identification of compounds are presented more conveniently on a logarithmic scale as spectra of relative retention volumes (or times) for volatile standard compounds (see Fig. 2). As Fig. 2 shows, polymers of rather similar structure are characterised by markedly different spectra. This form of presenting experimental results can be used in the future for compiling an atlas of spectra of standard volatile compounds on polymeric substances.

The RGC method has been developed in most detail for the characterisation (identification) of the asphaltenes (molecular weight 500–1000).[5] The so-called specific coefficients of interaction of volatile standard compounds with the stationary liquid phase I_g were used as characteristics of the asphaltenes:

$$I_g = 100 \lg (V_R^0/V_{RA}^0) = 100 \lg (V_g/V_{gA}) \quad (1)$$

where V_R^0 or V_g are the retention volumes of volatile standard on a column with asphalt, V_{RA} or V_{gA} the retention volumes of a hypothetical alkane, having the same molecular weight as the volatile standard being used. Recent investigation [13] showed the adequate constancy of I_g with respect to the principal parameters of the experiment.

Dorrence and Petersen [14] showed the advisability of using chemical reactions with the stationary liquid phase being investigated by RGC. To study the functional groups in the asphaltenes the specimen being studied in the column was subjected to silylation, as a result of which the active hydrogen atoms in the hydroxyl and carboxyl groups were replaced by trimethylsilyl radicals. Treatment of the asphaltene with *NN*-bis(trimethylsilyl)acetamide at 160°C led to a marked decrease in the specific interaction coefficients with selected volatile standards (phenol and propionic acid). This method can be used to characterise the functional groups of various polymeric compounds.

Table 1. Specific retention volumes of volatile compounds on polyglycols being used as stationary liquid phases (120°C; solid carrier: Celite 545).[10]

Polymeric stationary liquid phase	Specific retention volumes of the volatile compounds, ml g^{-1}								
	methanol	furan	hexane	ethyl acetate	cyclohexane	benzene	butanol	water	heptanol
Poly(propylene glycol) 1760	7.6	7.8	8.0	15.3	14.5	24.3	44.9	9.8	321
Poly(ethylene glycol) 1540	15.1	9.0	2.9	15.5	6.6	23.7	60.2	35.0	316

In conclusion, we note that when a packed column is used for the RGC method ~0.4 g of the test compound is required, but the amount is reduced to 3–4 mg when a capillary column is employed [5]. The use of the microversion of reversed chromatography is especially important for polymers which are difficult to prepare and in general for difficultly accessible compounds.

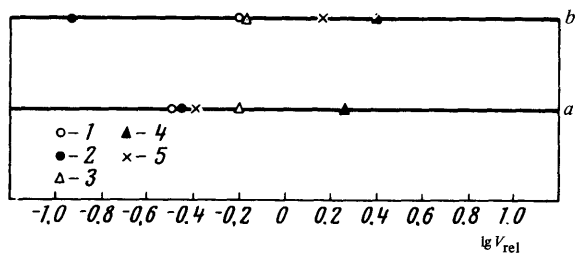


Figure 2. Chromatographic spectra of standard compounds on identifiable polymers: *a*) poly(propylene glycol) 1760; *b*) poly(ethylene glycol) 1540; *1*) methanol; *2*) hexane; *3*) ethyl acetate; *4*) butanol; *5*) water.

In view of the fact that the task of identification of the polymers sometimes reduces to the determination of their molecular weights, which is of interest in itself, we will examine how the retention of volatile compounds varies with the molecular weight of the polymer.

III. DETERMINATION OF THE MOLECULAR WEIGHT OF POLYMERS

A change in the molecular weight of a polymer leads to a change in many of its properties, and in particular in its chromatographic properties.

Evidently, the retention volume can be regarded as a colligative property of solutions, since its value is determined ultimately by the vapour pressure of the substances dissolved in the stationary liquid phase.

Like the other colligative properties of solutions (vapour pressure, freezing point depression, etc.), the retention volume of a dissolved substance depends upon the number of particles per unit volume of solution, and consequently on the molecular weight of the solvent [15] (the number-average molecular weight for a polydisperse polymeric liquid phase):

$$V_g^{(i)} = \frac{RT}{\overline{M}_n f_i^0 \gamma_i^\infty} \qquad (2)$$

where $V_g^{(i)}$ is the specific retention volume of the ith substance at column temperature T; f_i^0 and γ_i^∞ are the fugacity of the pure ith substance and its activity coefficient at infinite dilution in the stationary phase; $\overline{M}_n$ is the molecular weight of the stationary liquid, and R the gas constant.

However, as a strict analysis of the theory of dilute solutions [16] shows, only the molecular weight of the dissolved substance can be determined from the colligative properties of solutions, but not that of the solvent. This also applies to the retention volume. Actually, from the quantity Vg, which is readily determinable by experiment, only the product $\gamma_i^\infty \overline{M}_n$ can be calculated from Eqn. (1), and in all independent methods of determining γ_i^∞ a knowledge of the molecular weight of the solvent is always necessary.

Hence Eqn. (2) cannot be used for calculating the molecular weight of the stationary liquid. Nevertheless this equation is often used to determine γ_i^∞ and here $\overline{M}_n$ is usually taken as equal to the molecular weight of the monomeric form of the solvent, even when the latter is a strongly associated liquid.

Generally speaking, the values of γ_i^∞ or their variation with M_n needed for evaluating the molecular weight of the solvent by Eqn. (2), can be calculated theoretically. However, current theory of solutions does not in many instances yet permit the thermodynamic functions of the solution to be calculated with sufficient accuracy just from the molecular characteristics of the initial pure components, especially for polar associated substances. Usually, the theoretical expressions for the activity coefficients include parameters, the a priori evaluation of which is extremely difficult [17].

Consequently, semiempirical methods are often used for evaluating the quantities γ_i^∞ needed for the calculation of M_n by Eqn. (2).

Martire and Purnell [18] started from the well known Flory–Huggins [19] equation for the activity coefficient of the solvent in solutions of polymers and postulated its validity for limitingly concentrated (in relation to polymers) solutions:

$$\ln \gamma_i^\infty = \ln \frac{V_i^0}{V_p} + 1 - \frac{V_i^0}{V_p} + \chi, \qquad (3)$$

where V_P and V_i^0 are the molar volumes of the solvent (polymer) and of a low-molecular-weight solute respectively and χ is the Flory–Huggins interaction parameter. Then by assuming that within a polymer-homologous series the parameter χ is almost independent of $\overline{M}_n$ of its members, it is easy to use Eqns. (2) and (3) to calculate the molecular weight of the polymeric phase, if the retention volumes of a standard substance on this phase (index b) and on the same polymer with a known molecular weight (index a) are determined:

$$\frac{1}{\overline{M}_n^{(a)}} = \frac{\rho_a}{\rho_b \overline{M}_n^{(a)}} + \frac{\ln [(V_g^{(i)})_b / (V_g^{(i)})_a] + \ln (\rho_b / \rho_a)}{\rho_b V_i^0}, \qquad (4)$$

where ρ_a and ρ_b are the densities of phases a and b, and $\overline{M}_n^{(a)}$ and $\overline{M}_n^{(b)}$ are the number-average molecular weights of the polymers of phases a and b. Another, more convenient, modification of this method is the determination of the molecular weight of the polymeric stationary phase from the relative retention volumes of two substances of similar nature (often neighbouring members of a single homologous series), measured on phases a and b:

$$\frac{1}{\overline{M}_n^{(b)}} = \frac{\rho_b}{\rho_b \overline{M}_n^{(a)}} + \frac{\ln (R_a / R_b)}{\rho_b \Delta V_i^0}, \qquad (5)$$

where R_a and R_b are the relative retention volumes of two selected standard dissolved substances X and Y ($V_g^{(Y)} = 1$) on phases a and b:

$$\Delta V_i^0 = (V_i^0)_Y - (V_i^0)_X.$$

This method is usable for comparatively low-molecular-weight polymers—liquid silicones, polyglycols, and hydrocarbon oils with $\overline{M}_n \leqslant 1500$. The accuracy of the proposed method decreases as the molecular weight is raised.

The Flory–Huggins equation (3) and the assumption that χ is independent of the molecular weight of the polymer at a sufficiently high value are valid only in the absence of a specific interaction of the dissolved substance with the solvent. Hence the volatile compounds (solutes) used should preferably be saturated hydrocarbons.

Martire and Purnell [18] gave as an example the determination of the molecular weight of poly(propylene glycol) 1200 with the use of n-heptane and n-octane as volatile compounds and poly(propylene glycol) 400 as liquid phase of known molecular weight. The molecular weight of the poly(propylene glycol) calculated by Eqn. (5), was 1220 (according to the cryoscopic method, $\overline{M}_n = 1260$).

The use of the chromatographic method for determining the molecular weight of the stationary phase can naturally also be effected on a purely empirical basis by a preliminary calibration, that is, obtaining the graphical dependences of the retention volume on the molecular weight of the members of the polymer homologous series being studied.

The possibility of using this method was considered in several papers, for example, that of Kogan and Fedotova [20]. In this it was noted that with increase in the molecular weight of the oligomers containing –OH and –SH terminal polar groups and employed as the stationary phase the retention volumes of the non-polar compounds increase somewhat, whereas those of polar compounds (water, alcohols, ketones, ethers, etc.) fall considerably.

The effect of the molecular weight of poly(ethylene glycols) of the general formula $HO[CH_2CH_2O]_nCH_2CH_2OH$ on the retention indices of compounds of various types was also examined by Evans and Smith [21]. The most pronounced dependence of the retention volumes on the molecular weight of the polymeric stationary phases is observed for compounds capable of specific interaction with the terminal polar groups of polymers, for example, with the formation of hydrogen bonds. It was found that the retention volumes of such compounds depend linearly on the concentration of terminal functional groups in the polymeric molecule, that is, on the quantity $1/\overline{M}_n$, [22,23] where $\overline{M}_n$ is the molecular weight of the polymer.

The observed relations can be explained on the basis of the lattice theory of polymer solutions [19], which postulates

that long polymeric chains can be regarded as consisting of a set of segments—sections of the chain which are capable, because of the flexibility of the chain, of exchanging sites with the molecules of the second component of the solution and which occupy one cell of the quasicrystalline lattice of the liquid.

If we have a polymer with terminal polar functional groups the latter can, in accordance with the above ideas, be regarded as molecules of another component of the solution, since in their chemical behaviour (specific interaction with polar dissolved substances) they differ from all the other segments of the polymeric chains.

These predictions are justified, for example, by the fact that the reactivity of the terminal functional groups of macromolecules is often close to that of the same group in small molecules and does not depend on the size of the molecule [24].

In this instance a polymer with terminal functional groups, capable of reacting specifically with certain volatile compounds, can be regarded as a binary solution consisting of functional groups (solute) and of the remaining segments of the polymeric chains (solvent).

On the other hand, it is well known that when the stationary phase is a solution of a dissolved substance B, which reacts specifically with compound A, which is being passed through the column, then the distribution coefficient of compound A (K_A) depends on the concentration of substance B in the following manner [25]:

$$K_A = K_A^0(1 + K_x x_B), \qquad (6)$$

where K_X is the thermodynamic characteristic of the interaction of substances A and B, equal to the equilibrium constant of the reaction of complex formation A + B $\rightleftharpoons$ A.B, x_B the mole fraction of substance B in the stationary phase, and K_A^0 the distribution coefficient when $x_B \to 0$.

In the example being considered the functional groups play the part of the complex-forming agent B, and their mole fraction is $2m/\bar{M}_n$, where m is the molecular weight of the segment.

Hence

$$K_A = K_A^0\left(1 + K_x\frac{2m}{\bar{M}_n}\right) \qquad (7)$$

It is noteworthy that K_A^0 is in general also a function of the molecular weight owing to the contribution of the configuration term to the activity coefficient of the dissolved low-molecular-weight substance:

$$\left(\ln \gamma^{\infty}_{\text{config.}} = \ln\frac{V_i^0}{V_p} + 1 - \frac{V^0}{V_p}\right).$$

In this connection the relative retention volumes of the volatile compounds which react specifically with the functional groups of the polymers compared to the compounds incapable of such reaction (for example, saturated hydrocarbons) with approximately the same molar volume, will take into account to a considerable extent the change in the configuration entropy:

$$V_{\text{rel.}} = \frac{V_g^{(A)}}{V_g^{(\text{hyd})}} = \frac{K_A}{K_{\text{hyd}}} = \frac{K_A^0}{K_{\text{hyd}}}\left(1 + K_x\frac{2m}{\bar{M}_n}\right) \qquad (8)$$

Here K_{hyd} is the distribution coefficient of a hydrocarbon with a molar volume close to that of substance A.

Hence the relative retention volume for the standard volatile compounds which interact specifically with the terminal functional groups of the polymer is itself a more accurate linear function of $1/\bar{M}_n$.

On the basis of such ideas, a linear relation between V_{rel} and $1/\bar{M}_n$ was found earlier [23], but use of this equation did not reflect a specific interaction in the systems being considered. However, an equation of type (8) is valid only for such systems. Actually, as various investigations [18-20] have shown, V_g for saturated hydrocarbons varies with the molecular weight of the stationary phases by a different law.

It is interesting to note that Evans and Smith [21] observed a linear relation between the Kovačs retention indices (I) of polar compounds passing through a column and $1/\bar{M}_n$ for poly(ethylene glycols). The Kovačs index is known to depend linearly on the logarithm of the relative retention volume of the substance. Evidently, the linear dependence of I on $1/\bar{M}_n$ is the result of the fact that the quantity $K_X x_B$ in Eqn. (8) is rather low in comparison with 1 [$x_B < 0.2$; at a comparatively high temperature (100°C) the probability of the formation of hydrogen bonds becomes very slight and consequently K_X is small and probably even less than 1]. Then $\ln(1 + K_X x_B) \simeq K_X x_B$. A detailed experimental study of relations of the type of Eqn. (8) was made [22] in which specimens of poly(diethylene glycol maleate adipate) of various molecular weights were used as stationary phase and the chromatographed mixture contained ethanol, propanol, and benzene (internal standard).

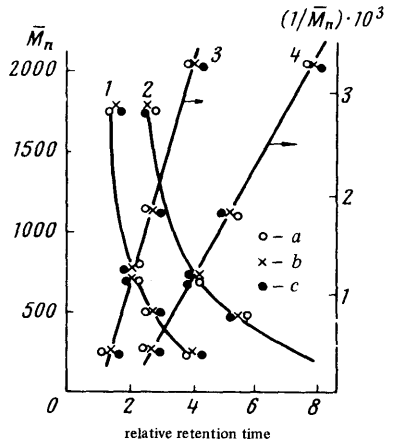


Figure 3. Variation of the relative retention times of ethanol (*1*, *3*) and propanol (*2*, *4*) (standard: benzene) with the molecular weight ($\bar{M}_n$) and the quantity $1/\bar{M}_n$ for poly(ethylene glycol maleate adipate): *a*), *b*), and *c*) series of experiments.

To reduce the adsorption effect of the carrier on the retention of polar alcohols the polyether being tested was carried on sodium chloride (0.25–0.5 mm fraction), proportion 1% of the carrier weight (column 200 × 0.4 cm, temperature of investigation 30°C). Fig. 3 shows the results for three series of experiments on the form of the variation of the relative retention time for ethanol and propanol with the molecular weight $\bar{M}_n$ and with $1/\bar{M}_n$. As Fig. 3 shows, the relative retention time of the volatile compounds which interact specifically with the terminal groups of the polymer depend linearly on the reciprocal

of its molecular weight. Naturally, to increase the sensitivity of the method the standard compounds used must be those having a strong specific interaction with the polar terminal groups of the polymer, that is, be characterised by very high values of K_X.

It was interesting to examine the effect of temperature on the parameters of Eqn.(8). It was to be expected that the first term of this equation should not depend significantly upon temperature, since it is linked with the non-specific interaction of the molecules of the volatile substances with the central fragments of the polymer molecule. For example, the second term of Eqn.(8), which reflects the specific interaction of a polar compound with the terminal groups of the polymer should depend on the temperature. To check these qualitative ideas, published results [10] were used to calculate the relative retention volumes of methanol (internal standard: decane) on poly(ethylene glycols) with molecular masses in the range from 300 to 6000 at 100° and 120°C. Fig. 4 shows the variation of the relative retention volume with the reciprocal of the molecular mass. In accordance with Eqn.(8), this relation is linear, with the first terms being almost the same for the two temperatures, but the second term decreasing as the temperature is raised.

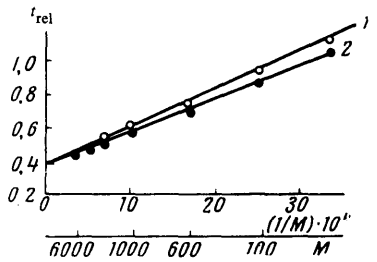


Figure 4. Variation of the relative retention volume of methyl alcohol with the reciprocal of the molecular weight of poly(ethylene glycol). Temperature, °C: *1*) 100; *2*) 120.

The relations found between the retention quantities for polymers with terminal functional groups which differ markedly from the main chain of the macromolecule can be used for polymers with number-average molecular weights up to 30 000–50 000.

The practical use of the chromatographic method is connected with the use of polymers of known molecular weight for a preliminary calibration. Several essentially positive features of the method are noteworthy. The carrying out of the experiment in a stream of carrier gas, the possibility of pre-heating the specimen, and performing the experiment at elevated temperatures considerably reduce the number of possible low-molecular-weight impurities, which usually impede the determination of the number-average molecular weight. Furthermore, the method is sensitive mainly to impurities which are capable of specific interactions with volatile substances of the standard mixture. We note that the possibility of determining the molecular weight of a series of oligomers with polar functional groups—poly(propylene glycols), poly(diethylene glycol adipates,) and thiokols—has been confirmed [20].

Kogan and Fedotova [20] have demonstrated another possible practical use of the variation of the retention of volatile substances with the molecular mass of oligomers. They showed that this relation can be used to select effective solvents for the fractionation of oligomers, since the solubility of the polymers and the retention volumes of the solvents are symbathically interconnected. For fractionation of oligomers a solvent must be chosen, the solubility in which of the members of the polymer homologous series shows the greatest dependence upon molecular weight. The use for this purpose of solvents and precipitants chosen on the basis of RGC results has given good results.

IV. INVESTIGATION OF THE THERMODYNAMICS OF THE INTERACTION OF VOLATILE COMPOUNDS WITH POLYMERIC COMPOUNDS

Even in the very beginning of the development of gas–liquid chromatography, one of its originators (Martin) noted the wide prospects of the use of the method for determining thermodynamic characteristics. He wrote [1]: "The method [of gas chromatography] provided perhaps the easiest of all means of studying the thermodynamics of the interaction of a volatile solute with a non-volatile solvent, and its potential value for providing this type of data should be very great". Thus position is also valid for polymeric compounds used as stationary phases.

An investigation by the gas-chromatographic method of the thermodynamic parameters for the interaction of low-molecular-weight compounds with polymers requires the calculation of a series of specific features for the behaviour of high-molecular-weight substances.

First of all it is necessary to note that the complexity of the molecular structure of polymeric materials leads to a variety of states in which the stationary polymeric phases can be found. Thus the polymers can be in two phase states—crystalline and amorphous, distinguished by differing degrees of ordering: long-range order in the arrangement of the links and chains for crystalline polymers and short-range order characteristic for liquid and amorphous solid polymers.

Solid polymers can also be partly crystalline, when crystalline and amorphous regions coexist in the polymer. In certain respects such a polymer can be regarded as an ordinary mixture of impermeable crystals and quasi-liquid amorphous medium [26].

Depending upon the temperature, amorphous polymers can be found in three physical states: vitreous, highly elastic, and visco-fluid distinguished by different degree of mobility of the structural elements of the macromolecules. The vitreous state is characterised solely by vibrational motion of the atoms which form the chain, in consequence of which the polymeric chain acquires the ability to buckle; the visco-fluid state by the mobility of all the macromolecules as a whole [27].

The mechanism of the retention (sorption) by polymeric molecules of low-molecular-weight compounds is determined by the phase and physical state of the polymers.

When the polymeric stationary phase is at a temperature below the glass temperature (T_g) the molecules of the specimen are not able to penetrate through the entire mass of the polymeric phase, and the retention here is determined by absorption on the polymeric surface, that is, gas-adsorption chromatography is involved. A similar situation is observed for crystalline polymers in the temperature range below the melting point.

Amorphous polymers at temperatures above T_g are capable both of dissolving low-molecular-weight compounds and of adsorbing them at the polymer–gas and polymer–solid carrier interfaces. When the high-molecular-weight phase is a partly crystalline polymer, then in the temperature range $T_g < T < T_f$ there is also the possibility of adsorption of the vapours of substances at the interfaces between the crystalline and amorphous regions.

In gas chromatography experimental methods for the determination of the contributions of each of the retention mechanisms to the total retention volume have been developed, and particularly methods of calculating retention due to dissolution of the substances in the stationary phase [28–30].

A knowledge of the retention volume due to dissolution of a substance permits the most important thermodynamic characteristics of the dissolution process to be calculated, namely, the distribution coefficient $k = V_g\rho$ (where ρ is the density of the stationary liquid phase), the activity coefficient γ_i [at infinite dilution, according to Eqn.(2)], and the changes in the excess partial molar thermodynamic functions of the solute [25]:

$$\Delta\bar{H} = R\frac{\partial \ln \gamma_i}{\partial\left(\frac{1}{T}\right)},\quad \Delta\bar{S} = -R\frac{\partial (T\ln\gamma_i)}{\partial T},\quad \Delta\bar{G} = -RT\ln\gamma_i.$$

Even the first studies of the thermodynamics of dissolution showed completely satisfactory agreement between the distribution coefficients for polymeric stationary phases determined by static and chromatographic methods. As an example, Table 2 gives results obtained by Anderson and Napier [31] for the distribution coefficients of benzene and cyclohexane in the gas–cresyl ester of poly(ethylene glycol) system.

Table 2. Distribution coefficients determined by static and gas-chromatographic methods for cresyl poly-(ethylene glycol) ether [31].

Compound	conditions					
	80°		100°		131°	
	GLC	static method	GLC	static method	GLC	static method
Benzene	71.6	73.0	43.4	44.1	23.4	20.1
Cyclohexane	18.9	19.9	13.5	15.0	9.3	7.8

The thermodynamic functions for the dissolution of volatile organic compounds were determined for several polymeric phases: Reopleks 400, poly(ethylene glycol) 600, Ftorsilikon FS-16, Silikon DS-550, [32] polyglycols [33,34], silicones [35], and solutions of magnesium chloride in poly-(ethylene glycol)-400. [36]

Problems in the use of gas chromatography for studying the thermodynamics of the interaction of a volatile substance with a polymeric phase were examined specially by Smidsrød and Guillet [37], who used Eqn.(2) to calculate from chromatographic results the coefficients γ_i^∞ for acetic acid, butanol, *o*-chloronaphthalene, naphthalene, and hexadecane in poly(*N*-isopropylacrylamide).

The excess thermodynamic functions for mixing at temperatures above the flow points of the polymer (Table 3) were calculated from the temperature dependences of γ_i^∞.

In calculating the activity coefficient from the chromatographic results by Eqn.(2), Smidsrød and Guillet [37] use the number-average molecular weight of the polymer; however, they note that for polymers some parameter determined by the size of the segment of the polymeric chain should be introduced instead of M_n. This indeterminacy disappears for the relative activity coefficients, which can also give valuable information in investigations of interactions of low-molecular-weight compounds with polymers [38].

Table 3. Excess thermodynamic functions for the mixing of volatile compounds of various types in poly(*N*-isopropylacrylamide), [38] temperature 200°C.

Compound	$\Delta\bar{G}$, cal mole^{-1}	$\Delta\bar{H}$, cal mole^{-1}	$\Delta\bar{S}$, cal deg^{-1} mole^{-1}
Acetic acid	−6740	−2400	+ 9.2
Butanol	−5390	+1100	+13.7
Naphthalene	−4360	+3900	+17.5
1-Chloronaphthalene	−4010	+3606	+11.3
n-Hexadecane	−1760	+2200	+ 8.4

The determination of the activity coefficients of low-molecular-weight compounds in polymers, especially under conditions of infinite dilution, is of considerable interest, especially for the theory of polymer solutions.

Thus the Flory–Huggins theory of regular solutions of polymers [19], which is based on a lattice model of liquids, allows the free energy of mixing in the dissolution of a long-chain polymeric molecule in a low-molecular-weight solvent to be calculated; for the case where the volume fraction of the polymer tends to 1 it yields Eqn.(3) for the activity coefficient of the substance dissolved in the polymer.

The first three terms on the right-hand side of Eqn.(3) are determined by the contribution from the changes in configurational or combinatorial entropy of mixing, due to the structure of the macromolecule (a flexible long chain, the segments of which are mobile and can exchange lattice sites with molecules of low-molecular-weight substances). Such a structure leads to large positive changes in entropy on the formation of polymer solutions and explains the characteristic negative departure from Raoult's law for the vapour pressure of the low-molecular-weight component of the solution.

The interaction parameter χ entering into Eqn.(3) reflects, in accordance with the theory of regular solutions, the contribution to the change in total free energy of dissolution of the change in free energy due to contact between the molecules of the components of the system. In the earlier stage of development of the theory of polymer solutions the interaction parameter χ was given the value of the van Laar enthalpy of mixing [19]:

$$\chi = \frac{V_i^0(\delta_i - \delta_p)^2}{RT}, \qquad (9)$$

where δ_p and δ_i are parameters of the solubility of the polymer and low-molecular-weight components of the solution respectively, in which δ_i is connected with the cohesion energy density $\Delta E_i^v/V_i^0$ by the relation

$$\delta_i = \left(\frac{\Delta E_i^v}{V_i^0}\right)^{1/2},$$

where ΔE_i^v is the heat of vaporisation of the pure ith component, and V_i^0 the molar volume of the ith component. However, the parameter χ is now regarded as a reduced

residual chemical potential consisting of enthalpy and entropy terms [39]:

$$\chi = \chi_H + \chi_S, \tag{10}$$

$$\chi_H = -T\left(\frac{\partial \chi}{\partial T}\right), \quad \chi_S = \frac{\partial(\chi T)}{\partial T}. \tag{11}$$

From the theory of regular solutions, the parameter χ is independent of the concentration of the solution. However, for many systems χ is a function of the composition of the solution and usually increases with the polymer concentration. Thus for the polyisobutylene–benzene system at 25 °C the parameter χ rises from 0.50 in the range of infinitely dilute solutions to 1.1 for $v_p \to 1$ (v_p is the volume fraction of the polymer) [39]. χ is exceptionally important in investigating solutions of polymers: it determines the solubility of the polymer, the critical compositions and temperature of the solutions as a function of the length of the molecule. Gas chromatographic measurements and application of Eqn. (2) enable the activity coefficient γ_i^∞ of the solute to be determined, and consequently the parameter χ for $v_p \to 1$:

$$\chi_{v_p \to 1} = \ln \gamma_i^\infty - \left(\ln \frac{V_i^0}{V_p} + 1 - \frac{V_i^0}{V_p}\right). \tag{12}$$

Values of χ_H and χ_S can be estimated from the temperature dependence of χ and Eqn. (11). Gas chromatography also allows the value of χ at finite concentrations of a low-molecular-weight solute to be calculated [40]. If the solution can be regarded as regular, it is easy to use Eqn. (9) and the values of χ to find the density of the energy of cohesion, an important characteristic of polymers. The change in χ with concentration and also the high value of the entropy constituent χ_S cannot be explained by the simple theory of regular solutions. There are now several other theories of solutions of polymers: Prigogine's theory of corresponding states [41] which takes account of the change in volume during dissolution; a theory using ideas of the theory of corresponding states and employing the equations of state of the pure components in the calculation of the characteristics (Flory theory) [39,42]; and various others.

Gas chromatography exhibits wide possibilities for the experimental verification of these theories.

A recent paper by Patterson and coworkers [43] examined the possibility of evaluating the interaction parameter χ as the most important thermodynamic characteristic of solutions of polymers directly from the retention volumes and not from γ_i^∞ to determine which it is necessary to know the number-average molecular weight of the polymeric liquid phase ($\overline{M}_n$). In this paper it was shown that:

$$\ln\left(\gamma_i^\infty \frac{\overline{M}_n}{M_i}\right) = \ln\left(\frac{a_i}{w_i}\right)^\infty = \ln\frac{v_i}{v_p} + \left(1 - \frac{V_i}{\overline{M}_p v_p}\right) + \chi =$$

$$= \ln\left[\frac{RT}{p_i^0 v_g^{(i)} M_i}\right] - \frac{p_i^0}{RT}(B_{ii} - V_i), \tag{13}$$

where v_i and v_p are the specific volumes of solute and polymer respectively; a_i and w_i the activity and weight fraction of solute; M_i is the molecular weight of the solute, p_i^0 the vapour pressure of the pure solute at temperature T; $p_i^0/RT(B_{ii} - V_i)$ a term allowing for the non-ideality of the gas phase, and B_{ii} the second virial coefficient of the pure ith solute. Consequently,

$$\chi = \ln\left[\frac{RTv_p}{p_i^0 V_g^{(i)} V_i}\right] - \left(1 - \frac{V_i}{\overline{M}_n v_p}\right) - \frac{p_i^0(B_{ii} - V_i)}{RT}. \tag{14}$$

At sufficiently large $\overline{M}_n$ the term $V_i/\overline{M}_n V_p$ can be neglected and then χ can be calculated without knowledge of the molecular weight of the polymer or its dispersion.

It was shown [45] that the change in the excess partial molar enthalpy of dissolution ($\Delta\overline{H}_i^\infty$) can be recalculated from the temperature dependence of χ after allowing for the temperature dependence of the molar volumes of the solute and polymer:

$$\Delta\overline{H}_i^\infty = RT^2(\alpha_p - \alpha_i) + R\left[\frac{\partial \chi}{\partial\left(\frac{1}{T}\right)}\right], \tag{15}$$

where α_i and α_p are the coefficients of thermal expansion of the components of the solution in the liquid state. The first term in $\Delta\overline{H}_i^\infty$, determined by the difference in the thermal expansion of the low-molecular-weight solute and the polymer, is ~100 cal at 300 °K.

Use of the Flory theory of solutions of polymers [42] leads to values of χ which differ greatly from the corresponding values calculated from the Flory–Huggins equation within the framework of the theory of regular solutions. It was found that the combinatorial part of the free energy of mixing is independent of the temperature and consequently

$$\Delta\overline{H}_i^\infty = R\left[\frac{\partial \chi^*}{\partial\left(\frac{1}{T}\right)}\right], \tag{16}$$

where χ^* is the interaction parameter calculated on the basis of the Flory theory.

Gas chromatography can be used extensively in the investigation of cross-linked polymers. From the statistical theory of the swelling of cross-linked polymers [19], at $v_p \to 1$,

$$\ln \gamma_i^\infty = \ln\frac{V_i^0}{V_p} + 1 - \frac{V_i^0}{V_p} + \chi + \frac{\rho_p V_i^0}{2M_c} \tag{17}$$

where V_p is the molar volume of the polymer before cross-linking, ρ_p the density of the polymer, M_c the molecular weight of the segment of the chain between the nodes of the lattice.

The parameter M_c, which is a characteristic of the density of the lattice and determines its strength, can thus be calculated from results of the chromatographic determination of γ_i^∞.

An investigation of the thermodynamics of the interaction of cross-linked polymers with low-molecular-weight compounds is of great interest in connection with the extensive use in chromatographic analysis of polymeric sorbents such as, for example, Porapak [44–46].

However, the use of gas chromatography for investigating solutions of polymers requires the investigation of a series of specific problems.

Primarily this is a problem of finding the gas–polymeric phase equilibrium under dynamic chromatographic conditions. The very high viscosity of the polymers, from 10^3 to 10^{13} P, should, at first glance, lead to the very slow diffusion of small molecules in the polymeric film, much slower than through a film of ordinary liquid.

However, only relatively non-coordinated movements of small segments of the polymeric chain are necessary for the diffusion of small molecules in a polymeric mass. In this connection the diffusion coefficients of low-molecular-weight substances are determined by the mobility of the segments and the packing density of the chains; here the molecular weight of the polymer is almost without effect on the rate of diffusion and the permeability through a film of polymer [26]. As a result, despite the enormous viscosity of the polymers the diffusion coefficients of small molecules in them are only one or two orders of

magnitude less than in ordinary liquids. Thus the diffusion coefficient of benzene in natural rubber is $D_{50°} = 3 \times 10^{-7}$ cm^2 s^{-1},[26] and for CO_2 in poly(methylsiloxane) rubber $D_{20°} = 3.8 \times 10^{-5}$ cm^2 s^{-1}.[27]

The high efficiency of the widely used chromatographic columns with polymeric liquid phases, for example, with silicone rubbers or poly(ethylene glycols) also shows that gas–polymer equilibrium is established rather rapidly under gas chromatographic conditions. However, in each instance of the study of the thermodynamics of polymer solutions by gas chromatography it is evidently necessary to prove that the measured retention volumes correspond to gas–polymer equilibrium. For example, it can be shown that the distribution coefficients K are independent of the carrier gas velocity.

An investigation of the rate of mass transfer in polymeric films is also of independent interest, since the permeability of the polymeric films for small molecules provides the basis of the technique of membrane separation of mixtures of substances[47].

Gas chromatography can be used to investigate the rate of mass transfer in liquid or amorphous films, from the variation of the height of the equivalent theoretical plate (HETP) with the velocity of the carrier gas[48].

The HETP equation allows the quantity d_L^2/D_L to be determined (where d_L is the thickness of the film of stationary liquid phase, and D_L the diffusion coefficient of the substance in the film); it is proportional to the so-called permeability lag time[26]. When d_L can be evaluated independently, the diffusion coefficient of the substance D_L can readily be determined from the lag time. The permeability P can be estimated from measurements of the distribution coefficients (K), which can be found from the retention volumes, and from the diffusion coefficients[26]:

$$P \equiv D_L \frac{K}{RT} . \qquad (18)$$

Incidentally, the parameter P can also be obtained directly from the component HETP, characterised by the erosion of the peak as a result of the resistance to mass exchange in the liquid phase (C_L):[48]

$$C_L \simeq \frac{K\frac{q_s}{q_m}}{\left(1+K\frac{q_s}{q_m}\right)^2}\frac{d_L^2}{D_L} \approx \frac{d_L^2}{K\frac{q_s}{q_m}D_L} \qquad (19)$$

for

$$K\frac{q_s}{q_m} \gg 1,$$

where q_S and q_m are the sections of the stationary and gas phases in the column respectively.

The use of gas chromatography in investigating diffusion in polymers and their permeability has a number of definite advantages over the usual methods of determining these quantities. These advantages are mainly connected with the rapidity and ease of the experiment, the availability of standard apparatus, and evidently, the adequate accuracy.

Another important feature is the above-mentioned variety of mechanisms of retention by polymeric phases, which act simultaneously in a chromatographic column.

As is known, important information about the retention mechanisms and the possibility of estimating the contribution of each mechanism to the total retention are given by the variation of the specific retention volumes with the amount of stationary phase in the column[28,29].

In the determination of retention volumes on polymeric phases an appreciable dependence of the retention volume on the size of the specimen even for very small specimens is often observed. Thus, Lavoie and Guillet[49] observed a dependence of V_g on the size of the specimen in the range 0.1–1 μl and evidently only for specimens of ~0.01 μl does Henry's law cease to be obeyed, from which the independence of V_g and the size of the specimen also follows.

The non-linearity of the distribution isotherms even in the range of very small concentrations (low volume fraction of the low-molecular-weight component, but nevertheless the mole fraction can be very large) can in many instances be explained by the sorbed molecules (especially the vapours of poor solvents) having a tendency to form aggregates inside the polymers[26]. It is therefore to be expected that the worse the dissolving ability of the sorbate, the narrower the range of concentrations where the distribution isotherm is close to linear. This conclusion is confirmed, for example, by results[37] where the greatest dependence of the retention volume on the size of the specimen was observed for the peaks of hexadecane, which is a very bad solvent for the polymeric phase, poly(*N*-isopropylacrylamide).

The values of V_g used to calculate the thermodynamic characteristics of the distribution, have been obtained by extrapolating to zero size the experimental relations between V_g and the size of the specimen.

Methods have now been developed for the chromatographic investigation of the thermodynamic parameters for the distribution at the terminal concentrations of sorbed substances and in particular methods of determining distribution isotherms[40] and the specific surfaces of the stationary phase[25], which can undoubtedly be also used for polymeric phases.

These methods are undoubtedly widely used in studying the permeability, swelling, and plasticising of polymers.

V. STUDY OF PHASE TRANSFORMATIONS

A phase transformation converts the initial stationary phase into a new non-stationary phase (new sorbent), which is in general characterised by physicochemical properties different from those of the initial phase. This should be reflected by a change in the chromatographic characteristics of volatile standard substances in the range of the phase transformation of the stationary phase. Therefore the RGC method can be used for studying phase transformations in polymers. In studying phase transformations it is desirable to use as chromatographic characteristics not only the retention volume or time, but also the width of the peak of a volatile standard compound[7].

The marked dependence of the retention parameters on temperature in the range of fusion of the stationary liquid phase was noted long ago[50–55]. However, usually the investigators were interested not in studying the phase transformation phenomenon but in its effect or use in analytical chromatography. Thus the pronounced decrease in the retention of the compounds being analysed on eicosane when the column is cooled to a temperature below its melting point has been used[50] as a method of rapid elution from the column of heavy hydrocarbons after the analysis of the lighter components.

Evidently the first studies in which the chromatographic properties of stationary phases were specially investigated in the range of their phase transformations were those of liquid crystals (as stationary liquid phases)[6,56,57]. The stationary liquid phases found in a liquid-crystalline state are very selective for the separation of the isomers of organic compounds (for example, *o*-, *m*-, and *p*-cresols).

At the temperatures of the phase transformations from the crystalline state to the mesomorphic liquid-crystal, and also in going from the mesomorphic to the isotropic liquid state sharp anomalous changes in the specific retention volume are observed.

As shown by Alishoev and coworkers [7] the RGC method can also be used successfully in studying the phase transformations on going from one crystalline modification to another by the example of carbon tetrachloride. Subsequently this method was used successfully by Guran and Rodgers for investigating phase transformations in crystals of thallium nitrate [58], Cu_2HgI_4, and Ag_2HgI_4. [59] In all the above instances the results of the gas-chromatographic experiment agree well with those on phase transformations obtained by other methods.

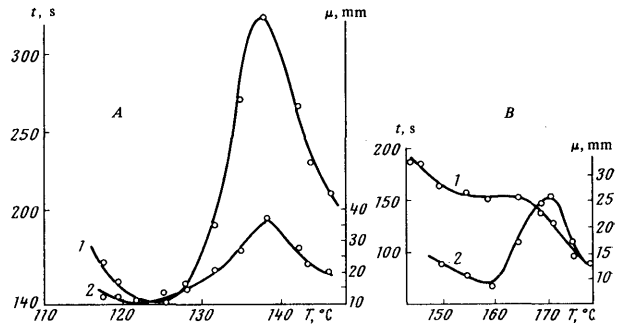


Figure 5. Variation of the retention time (*1*) and peak width (*2*) with the column temperature: *A*) the n-tetradecane–polyethylene system; *B*) the cetene–polypropene system.

According to Berezkin and coworkers [60], the RGC method was first used specially for studying phase transformations in polymers by Alishoev and coworkers [7], who investigated stereoregular polymers with a high degree of crystallinity: polyethylene and polypropylene. A mechanical mixture of powders of the test polymer (1%) with glass spheres was put in a column (100 × 0.4 cm) which was connected to a chromatograph and heated at a rate of 0.2–0.5 deg min^{-1}. Periodically a specimen of standard substance was introduced into the column and its chromatogram recorded. The results of the experiments were presented as graphs of the retention time and peak width of the standard substance (for polyethylene–tetradecane and polypropylene–cetene) against column temperature (Fig. 5). [7] In the instances investigated the retention time and peak width curves show a maximum (a plateau on the cetene retention time curve for polypropylene) in the temperature range of the phase transformation. The appearance of maxima is due to a change in the distribution constant and diffusion coefficients of the standard volatile substance as a result of the phase transformation. In the deposition of polypropylene on glass spheres from its solution in decalin at 110°C or from a melt in an inert atmosphere the plateau on the curve in this coordinate system associated with the phase transformation almost disappears. Similar behaviour is noted in studying phase transformations of thallium(I) nitrate crystals [58].

Guillet and coworkers [37,49,61–63] have made a large contribution to the development of the RGC method in studying phase transformations in high-molecular-weight compounds and their quantitative interpretation.

In these studies the variation of $\lg V_g$ with the reciprocal of the temperature was examined for polymeric stationary phases. Fig. 6 shows the most general type of this relation for the semicrystalline polymer [64]. Such behaviour is characteristic, for example, of polypropylene and crystalline polystyrene when hydrocarbons (n-alkanes) are used as solutes.

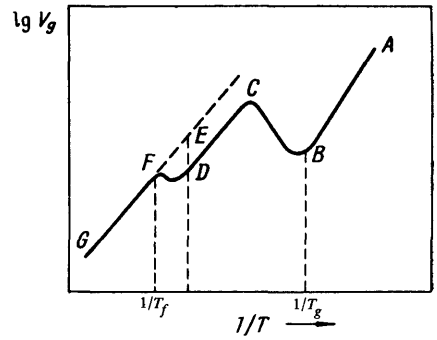


Figure 6. Variation of the retention volume with the reciprocal of the absolute temperature of the column for semicrystalline polymers.

In the range corresponding to the part *AB* of the curve the polymer is at temperatures below the glass point. The retention is here determined by adsorption on the surface of the vitreous polymer, since the molecules of the specimen cannot penetrate into the body of the polymeric film.

The linear dependence of $\lg V_g$ on $1/T$ is observed up to the glass point (T_g) (point *B*). An increase in the retention volume at the phase transformation point, also observed for phase transformations of the first type [55], is, as already noted, due to a fundamental change in the structure of the stationary phase. A further rise in temperature leads to passage of the curve through a minimum and to an increase in $\lg V_g$ along the part *BC*. Guillet [62] explains this increase as follows. The region *BC* corresponds to non-equilibrium adsorption of the vapour on the polymeric phase. The molecules start to penetrate into the body of the phase but the diffusion rate is so small that only at point *C* does the adsorption of vapour reach the entire thickness of the film in the contact time. This prediction could readily be checked from results on the variation of V_g with gas velocity. However, the studies of the behaviour of stationary phases close to the transformation point do not include such results.

The possibility of chain flexibility (progressive movement of the segments) in the amorphous ranges of polymers is known to increase with the temperature. In addition, an increase in the temperature leads to breakdown of ordered supermolecular structures (blocks) and the molecules acquire the conformation of disordered convoluted and tangled balls [64]. In other words, raising the temperature leads to a decrease in the mean cohesion energy of the molecules of amorphous polymers, which should, in turn,

lead to a decrease in the activity coefficient of the solutes—compare, for example, Eqns.(9) and (3). It seems that these changes in the cohesion energy are most pronounced in the region *BC* of the curve (Fig. 6).

Thus the increase in V_g with temperature is explained by the fact that in the range *BC* as the temperature is raised the activity coefficients γ^{∞} of the solutes decrease more sharply than the vapour pressure of the vapour of the pure solutes p_1^0 or f_1^0 of Eqn.(2) increases.

The definition and depth of the minimum on the curve (Fig. 6) depend on the nature and dimensions of the molecules of the volatile solutes. Thus it has been shown [38] that for butanol and acetic acid the graph of $\lg V_g$ against $1/T$ for the stationary phase poly(*N*-isopropylacrylamide) is a straight line over the entire temperature range. Possibly the formation of strong hydrogen bonds by the molecules of the alcohol and acid with the amide group of the polymer makes the mechanism of their dissolution in the polymer differ from that for hydrocarbons.

Nevertheless it should be noted that the nature of the inflection on the graph of $\lg V_g$ against $1/T$ close to the glass temperature and the dependence of its form on the nature and size of the sorbate molecules are still far from explained.

At point *C*, an amorphous polymer or an amorphous part of a semicrystalline polymer evidently reaches a state which is identical with that of ordinary liquids. Thus, for poly(*N*-isopropylacrylamide) point *C* is close to its flow point. Thus along the segment *CD* in addition to possible adsorption at the surface and at the boundaries of the amorphous and crystalline regions, dissolution of the vapours of the volatile compounds takes place over the entire volume of the amorphous part of the polymer. In this region the thermodynamic functions of the dissolution can be determined.

Close to point *F* the crystalline part of the polymer melts. In this region a characteristic maximum is usually observed on the curve (Fig. 6). [55,63] The range *FG* corresponds to the state when the entire mass of the polymer participates in the dissolution of the molecules of the specimen. Since it is thought that on the segment *CD* the crystalline regions of the polymer do not participate in the retention of the solute molecules, it is possible to estimate the degree of crystallinity of the specimen in the temperature range *CD*. Actually, extrapolation of the line *FG* in the range of temperatures below T_f allow the retention volume which would correspond to a hypothetical amorphous state of the entire polymer at $T < T_f$ to be estimated. Then the degree of crystallinity can be calculated from the formula:

$$\text{degree of crystallinity} = \frac{(V_g)_E - (V_g)_D}{(V_g)_E} \cdot 100 \qquad (20)$$

(see Fig. 6).

In this the possibility of adsorption of the volatile standards at the boundary between the crystalline and amorphous parts or at the gas–polymer and polymer–solid carrier surfaces is not taken into account.

Guillet has termed the method of investigating the structure and physical state of polymers from the temperature dependence of the retention volumes the method of "molecular specimens" [62].

This method has been used for determining the degree of crystallinity of high-density polyethylene at various temperatures [63]. Fig. 7 shows the variation of its degree of crystallinity with temperature obtained gas-chromatographically and by differential thermal analysis. As Fig. 7 shows, the agreement between the two methods is completely satisfactory.

As the form of the curve in Fig. 6 shows, the variation of $\lg V_g$ with $1/T$ can be used to determine the glass point of the polymers.

Table 4 [49] shows values of T_g obtained by differential thermal analysis and by reversed chromatography. The agreement between the two methods is completely satisfactory and evidently in determining T_g of the polymer by gas-chromatography it is desirable to use as characteristic quantity the temperature (T_1) of the first departure from linearity on the curve of the logarithm of the retention volume against the reciprocal of the temperature.

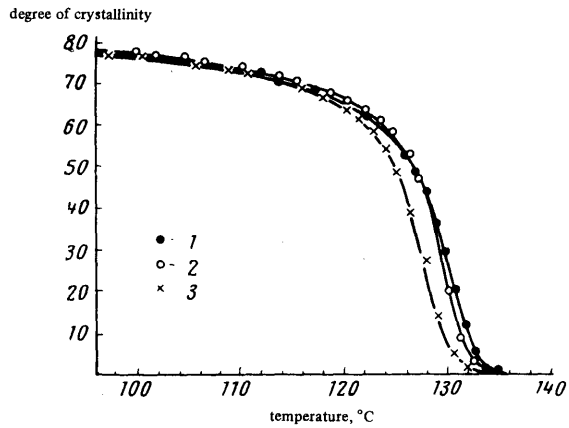


Figure 7. Variation of the degree of crystallinity of high-density polyethylene with the temperature: *1*) Calorimetric results; *2*) and *3*) results obtained by the method of molecular specimens; *2*) on cooling at a rate of 1.0 deg min^{-1} and heating at 0.5 deg min^{-1}; *3*) on cooling according to the ballistic rule and heating at 0.5 deg min^{-1}.

Table 4. Determination of the glass temperature by the reverse gas chromatographic method [49].

Characteristic	Poly (vinyl chloride)		Polystyrene	Poly(methyl methacrylate)
	A	B		
Molecular weight	68 000	35 500	31 000	48 000
Standard volatile component	dodecane	dodecane	dodecane	hexadecane
Glass temperature, °C (DTA)	75±2	75±2	95±2	100±2
Temperature for the first departure from linearity, T_1, °C	81	81	88	97
Temperature of first minimum, T_2, °C	91	91	100	105

The RGC method has also been used successfully for studying the kinetics of the crystallisation of organic substances from the melt. The use of this method for polymeric compounds has been described by Guillet and

coworkers[63], and for monomeric compounds by Andreev and coworkers[65].

The features of the reversed chromatography method in the study of phase transformations are the relative simplicity of the apparatus and experimental procedure, the possibility of rapid measurement of the chromatographic characteristics for volatile standard substances of various types and the use of small amounts of the polymers being tested. Another advantage of the RGC method in comparison with widely used methods based on measuring the heat of phase transformation is the possibility of studying slow phase transformations.

VI. INVESTIGATION OF THE KINETICS OF THE REACTIONS OF POLYMERS

In studying the kinetics of chemical reactions by the RGC method the reaction is effected in a chromatographic column where the reaction mixture is used as stationary phase for a standard mixture of volatile non-reacting compounds. The change in the composition of the reaction mixture with time is determined by periodic measurement of the elution characteristics of the volatile standards. The determination of the composition of the reacting system with time is based on the use of a relation of the type

$$c_i = f(V_j), \qquad (21)$$

where c_i is the concentration of one of the components in the reaction mixture, V_j the retention volume of one of the standards. The concept of "component" also embraces the functional groups of the polymer being tested.

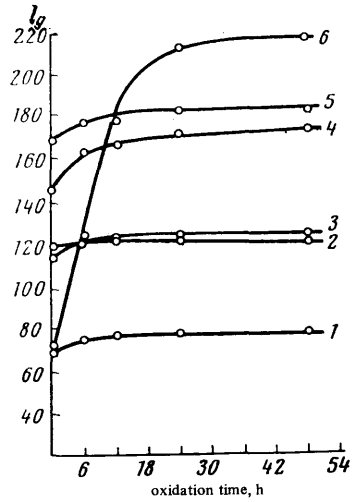


Figure 8. Change in the interaction coefficients during the oxidation of asphaltene: *1*) butanol; *2*) propionic acid; *3*) pyrrole; *4*) phenol; *5*) formamide; *6*) 1-methylpyrrolidone.

This method requires small amounts of the test substances and is characterised by the following advantages: a thin film of the phase allows the kinetic regime to be realised readily, an investigation of the kinetics of the reaction can be made without removal of specimens, and it is possible to investigate the kinetics of reaction systems which cannot be analysed chromatographically. The method was proposed by Berezkin and coworkers[60] and used for studying the kinetics of oxidation of benzaldehyde into benzoic acid[66]. It was shown that the oxidation of benzaldehyde by atmospheric oxygen (air is a carrier gas) proceeds formally by a first-order reaction, and the rate constant obtained in a chromatographic experiment differs from that obtained in a bubbling reactor by no more than 3%.

This method was subsequently used by Davis and Petersen for studying the oxidation of asphaltene[67]. Fig. 8 shows the change in the specific interaction coefficient — see Eqn. (1) — for various volatile standards as a function of the time of oxidation of the asphaltene with air at 130°C.

Undoubtedly, the RGC method is extremely convenient for studying the kinetics of the reactions of polymeric compounds.

In conclusion, we wish to emphasise that although the development of the RGC method is far from ended the experience that has already been accumulated is sufficient for the wide use of this method in polymer chemistry for solving the most diverse problems.

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