PAVEL KRATOCHVÍL[*], JAROSLAV STEJSKAL

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic
Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

Chemical heterogeneity of copolymers and its characterization

Summary — The heterogeneity of copolymers in chemical composition is overviewed qualitatively. The following topics are discussed: the non-uniformity of copolymers and its description; the heterogeneity of statistical and block copolymers; the effect of chemical heterogeneity on the properties of copolymers; the methods used to characterize chemically heterogeneous copolymers; size-exclusion chromatography (SEC) of copolymers involving concentration and composition detection; SEC with on-line concentration and light-scattering detection; and the calculation of the distribution functions of chemically heterogeneous copolymers based on the operating parameters of synthesis.

Key words: statistical copolymers, block and graft copolymers, chemical heterogeneity, chemical composition distribution, methods for characterization of chemically heterogeneous copolymers

Every copolymer substance comprises macromolecules differing not only in molecular weight but also in chemical composition. Thus, each copolymer is non-uniform in both molecular weight and chemical composition. The non-uniformity in composition is usually referred to as the chemical heterogeneity, or heterogeneity in chemical composition, of copolymers. The present paper overviews this problem qualitatively.

DESCRIPTION OF NON-UNIFORMITY OF COPOLYMERS

A complete description of a non-uniform binary copolymer is presented by a two-dimensional distribution function, $w(M, x)$, giving the mass fraction of molecules with molecular weight M and chemical composition x, which is expressed as a mass fraction of monomeric units of one of the two types present (Fig. 1). The cross-sections through the distribution function cut by the planes perpendicular to the axis of composition or molecular weight yield the distribution functions of molecular weight at specific compositions, $w(M, x_i)$, or the distribution functions of chemical composition at particular values of molecular weight, $w(M_j, x)$.

Two marginal distribution functions are important characteristics of a non-uniform copolymer, viz., the marginal distribution function of molecular weight, $w(M)$, and the marginal distribution function of chemical composition, $w(x)$, giving, respectively, the mass
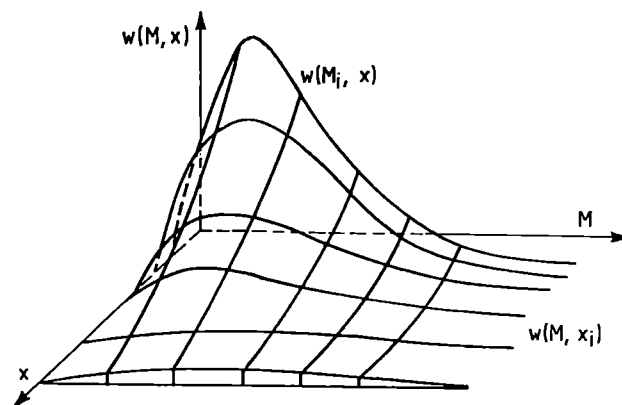

Fig. 1. Two-dimensional differential distribution function $w(M, x)$ of molecular weight M and of chemical composition x

fraction of molecules with a particular value of molecular weight, irrespective of chemical composition, and the mass fraction of molecules with identical composition, irrespective of molecular weight.

Analytical expressions for the above distribution functions and various types of copolymers and copolymerization mechanisms have been derived and seem to describe satisfactorily the real distributions [1—6 and refs. cited therein]. Direct single-step experimental determination of complete two-dimensional distribution functions is mostly not feasible. It would be desirable to have a technique capable of isolating copolymer molecules with a particular molecular weight and composition. In principle, mass spectrometry could meet this

*) To whom all correspondence should be sent. Phone: +420-2-2040-3277; fax: +420-2-3535-7981; e-mail: krat@imc.cas.cz

requirement [7]. In the present state of the art, however, mass spectrometry is far from being a universally applicable method for a single-step determination of the two-dimensional distribution function of copolymers. Both M and x simultaneously affect each separation mechanism available at the present time for fractionation of copolymers, and the resulting fractions are mixtures of molecules with various combinations of molecular weight and composition. But a better or poorer approximation to the distribution function of the type $w(M, x_i)$, $w(M_j, x)$, $w(M)$, or $w(x)$ is often accessible experimentally by the use of the techniques mentioned below.

HETEROGENEITY OF STATISTICAL COPOLYMERS

In the copolymerizations of two or more monomers, two mechanisms generating chemical heterogeneity of the resulting statistical copolymers are operative. The first, leading to what is usually called instantaneous heterogeneity, is active at any conversion. Owing to their statistical nature, the copolymerization reactions yield molecules with non-identical composition. Intuitively, one would guess that the effect of this mechanism is strong with molecules at low degrees of polymerization. For example, in codimerization of monomers A and B, mostly non-negligible amounts of all three possible types of molecules, viz., A_2, AB and B_2, result. As the degree of polymerization is increased, the formation of molecules with extremely different compositions is less and less probable and one would expect the distribution function of chemical composition to become narrower. Indeed, it has been shown rigorously that the width of the distribution function of chemical composition of statistical copolymers decreases as the degree of polymerization is increased and becomes infinitely narrow, actually a delta function, at infinitely high degrees of polymerization [5, 8].

The other mechanism gives rise to the so-called conversion heterogeneity of statistical copolymers [9]. Since the reactivities of comonomers are different, the composition of the monomer mixture shifts as the conversion progresses and the composition of copolymer molecules formed at various stages of the copolymerization reaction changes accordingly. Clearly, the effect is small at low degrees of conversion and becomes more and more important as conversion proceeds [8, 10]. The effect is not operative at the azeotropic compositions of monomer mixtures and in the rather seldom case when both monomer reactivity ratios are unity, $r_A = r_B = 1$.

Let us assume a simple model of a copolymerization reaction in which the monomer reactivity ratios are constant, the penultimate-unit effect is negligible and the activity coefficients of all components of the reaction mixture are unity, i.e., activities can be replaced by amount-of-substance concentrations. Then, it is relatively easy to calculate the distribution function of chemical com-

position, which for binary copolymerizations depends on the following quantities: the ratio of amount-of-substance concentrations of monomers, monomer reactivity ratios, and degree of conversion [8, 11].
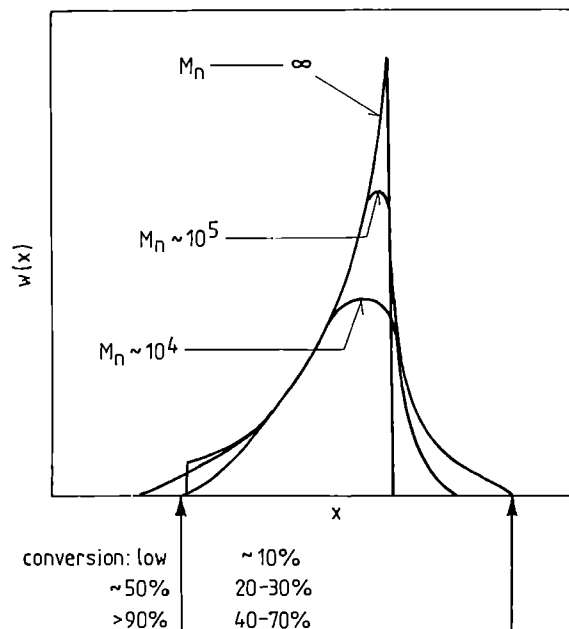
Figure 2 gives a rough idea of what typical distribu-

Fig. 2. Chemical composition distribution $w(x)$ for statistical copolymers of various number-average molecular weights M_n

tion functions of chemical composition, $w(x)$, for statistical copolymers look like. The range of compositions of copolymer molecules present in a copolymer is for conversions of a few per cent some 10%, for medium conversions 20—30% and for high conversions 40—70%. Statistical copolymers with predetermined chemical composition distribution or chemically homogeneous copolymers can be obtained by modifying the copolymerization process, e.g., by adding a monomer mixture of appropriately varying or constant composition [12].

When low-molecular-weight monomers are copolymerized with macromonomers, well-defined graft copolymers are produced. Since the molecular weights of the constitutional units are highly different, the mathematical apparatus describing the chemical heterogeneity [13] as well as the experimental approaches to its characterization [14, 15] have to be modified.

HETEROGENEITY OF BLOCK COPOLYMERS

It seems to be generally assumed that block copolymers with a narrow molecular weight distribution (MWD), prepared, e.g., by exacting anionic polymerization, have also a narrow distribution function of chemical composition. This may or may not be true. From the statistical point of view, the formation of block copoly-

mers can be treated as the combination of blocks of different types. The blocks always have some, even if narrow, MWD. In the formation of two-block copolymer molecules with blocks of type A and B, a long block A can combine with a short block B. Another short block A joins a long block B. The two copolymer molecules may have the same molecular weight and yet differ considerably in chemical composition. This simple schematic argument indicates that block copolymers with narrow MWD can have a non-negligibly broad distribution in chemical composition.

A rigorous quantitative analysis of the problem of chemical heterogeneity of block copolymers shows [4, 16—18] that, indeed, they often have a broad distribution in chemical composition although their MWD is quite narrow. The decisive factor for the width of the distribution function of chemical composition of block copolymers turns out to be the width of the MWD of the constituent blocks, actually the weight-to-number-average molecular weight ratio, $\overline{M}_w / \overline{M}_n$, virtually irrespective of the type of the MWD function.

As an example, let us examine the distribution functions of chemical composition of a two-block copolymer in which the mass fractions of monomeric units of both types are equal, i.e., $x = 0.5$ (Fig. 3) [16]. Even if the
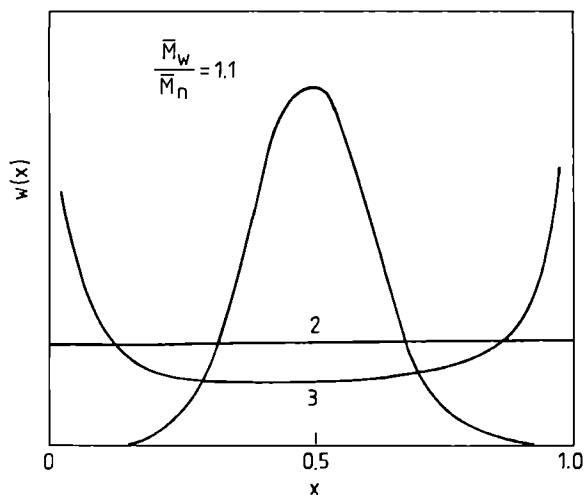

Fig. 3. Chemical composition distribution $w(x)$ of a diblock copolymer composed of blocks having an equal number-average molecular weight and various weight-to-number-average molecular weight ratios $\overline{M}_w / \overline{M}_n$ is equal: 1 — 1.1; 2 — 2; 3 — >2

MWD of each type of blocks is narrow, e.g., $\overline{M}_w / \overline{M}_n$ = 1.1, non-negligible amounts of copolymer molecules differing in composition by as much as fifty per cent are present. The width of the distribution function of chemical composition increases with increasing value of the $\overline{M}_w / \overline{M}_n$ ratio. At $\overline{M}_w / \overline{M}_n$ = 2, a rectangular distribution results. This means that, in the copolymer, equal mass fractions of molecules are present with the compo-

sitions ranging from one homopolymer over all possible copolymer compositions up to the second homopolymer. For $\overline{M}_w / \overline{M}_n$ > 2, the distribution function of chemical composition assumes a U-shaped form. In such block copolymers, considerable mass fractions of molecules can be found with compositions close to either homopolymer, whereas the mass fraction of molecules with composition corresponding to the average composition, i.e., composition determined by any analytical technique, is small.

The important message of this section is that block copolymers are likely to have a perceivable distribution of chemical composition. The potentially complicating effect of chemical heterogeneity on the behavior of block copolymers would mostly not be considered.

EFFECT OF CHEMICAL HETEROGENEITY ON COPOLYMER PROPERTIES

To the best of our knowledge, there are no detailed systematic studies on the effect of chemical heterogeneity of copolymers on their properties. The available fractional evidence, however, enables us to draw a few qualitative generalizing conclusions.

With statistical copolymers, experimental data indicate the following: as long as the distribution of chemical composition is such that all the molecular species present are compatible and the bulk copolymer is just a single phase, the effect of heterogeneity on properties is moderate [19], if any. In copolymers containing fractions with compositions so different that they are no more compatible [20, 21], phase separation may occur in the bulk state and the multi-phase structure of the material affects perceivably its properties [22]. This occurs quite often when two monomers with low values of both monomer reactivity ratios are copolymerized to high conversions and the initial composition of the monomer mixture is far from the azeotropic composition [11]. At some conversion, one of the monomers is virtually depleted and the macromolecules form the composition of which is close to the composition of the homopolymer of the abundant monomer. In statistical copolymers of which one corresponding homopolymer is crystalline and the other amorphous, chemical heterogeneity produces an effect on the degree of crystallization and, consequently, on properties. In block [23—27], segmented [28, 29] and graft [13, 14, 30] copolymers, chemical heterogeneity also modifies their morphology, processing and properties.

Chemical heterogeneity plays a significant role in linear low-density polyethylene (LLDPE) [31]. This important commodity polymer is a statistical copolymer of ethylene and an α-olefin, usually C_4—C_8. For its production, the Ziegler—Natta type catalysts are mostly used. These catalysts are known to comprise a plurality of types of active centers differing in their ability to incorporate various monomers in the growing polymer

chains. On centers readily adding the α-olefin molecules, the termination reaction is fast and copolymer molecules rich in α-olefin monomeric units have a low molecular weight. On the other hand, on the centers reluctant to incorporate α-olefins, the growing chains terminate slowly and the resulting high-molecular-weight portions of the copolymer show a low or even zero content of α-olefin monomer units. LLDPE is an example of a copolymer with a pronounced interdependence of molecular weight and chemical composition. The extent of heterogeneity affects the crystallinity, morphology and properties of LLDPE.

METHODS FOR CHARACTERIZATION OF CHEMICALLY HETEROGENEOUS COPOLYMERS

The spectrum of experimental techniques used for characterization of chemically heterogeneous copolymers is relatively broad. Several features are common to all those techniques: (i) each has a limited applicability; none can be successfully used with every copolymer; (ii) to obtain reliable results, each method must be operated at the top degree of performance because, as a rule, chemical heterogeneity does not manifest itself conspicuously in a particular property or process; (iii) to find experimental conditions suitable for characterization of a specific type of copolymer is mostly difficult and time-consuming. The potentials of the individual techniques are briefly mentioned below.

The first attempts to characterize chemical heterogeneity of copolymers were made by using the fractionation techniques based on phase separation, in particular precipitation or extraction fractionation [32 and refs. cited therein]. The procedures utilize the fact that the solubility of copolymers is a function of chemical composition and molecular weight. Solvent—precipitant systems can be found in which the phase separation is affected more either by chemical composition or molecular weight but, always, both factors operate simultaneously [14]. Fractions thus obtained are more uniform in composition or molecular weight, or both, than the original copolymer but still too non-uniform to enable the distribution function of molecular weight or chemical composition to be accurately determined. The distribution thus determined is always narrower than the true one, on account of the limited efficiency of separation. Nowadays, the phase separation techniques are employed for preparative purposes if large amounts of copolymers with acceptable uniformity with respect to chemical composition or molecular weight, or both, are needed.

A fractionation procedure using demixing solvents is applicable especially to block and graft copolymers [6, 13, 14, 33]. Two solvents of limited miscibility are selected so that one type of the blocks is preferentially soluble in one phase, whereas the other in the second phase. Changing the temperature allows to modify the compo-

sition of the coexisting phases and the distribution of the copolymer between the two phases which makes its fractionation possible. This experimental approach is particularly suitable for the separation of homopolymer admixtures from block and graft copolymers.

A novel method utilizing phase equilibria for fractionation of non-uniform polymers or copolymers according to the ability of their macromolecules to crystallize is the temperature rising elution fractionation (TREF) [34—36]. At the present time, TREF is widely used for characterization of polyolefins [37] and copolymers of olefins. The method is based on the following principle: lowering the temperature of the solution of a crystalline polymer makes the polymer deposit on an inert support, e.g., glass beads, in layers comprising molecules of the decreasing ability to crystallize. In the second phase, the temperature gradually increases and the layers dissolve in the reverse order, i.e., those with the lowest melting temperature and lowest crystallinity first, and gradually the layers with higher melting temperatures and degrees of crystallinity are dissolved. The primary data is the distribution curve of melting temperatures. Analysis of the fractions, e.g., by NMR, yields information such as composition of copolymers or degree of stereoregularity in polymers with configurational repeating units.

The distribution function of chemical composition, $w(x)$, of statistical copolymers can be obtained by measuring the change in the average composition of a copolymer or residual monomer mixture following the conversion [38]. Just a material balance enables this dependence to be transformed into the distribution function of chemical composition. Typically, the average composition of a statistical copolymer changes between the start of polymerization and the complete conversion, depending on monomers, their reactivity ratios and the ratio of monomer concentrations at the beginning of the reaction, from a few to 10—15%. The crucial problem in the application of this conceptually simple and rigorous method is the requirement of a very precise measurement of small shifts in the average composition of the copolymer or residual monomer mixture. For a tolerably accurate determination of the distribution function, the analytical technique must be able to perceive differences in composition of a tenth or even hundredth of a per cent, depending on the overall change of composition, and this is by no means easy.

With some copolymers, their heterogeneity in composition can be characterized by light scattering from dilute solutions [39, 40]. From the scattering intensities of copolymer solutions in at least three solvents with sufficiently different refractive indices, two parameters characterizing the chemical heterogeneity can be obtained in addition to the true value of the weight-average molecular weight. One of them reflects the width of the distribution of chemical composition of the copolymer while the other indicates the presence or absence of interdependence between molecular weight and composition. Light scattering yields reasonably reliable values

of the heterogeneity parameters only under a number of restrictive conditions, *viz.*, the components of the copolymer have sufficiently different refractive indices, the distribution of chemical composition is relatively broad, and the molecular weight is rather high, say $3 \cdot 10^5$, or better more.

In the past, ultracentrifugation in a density gradient was used to prove chemical heterogeneity of copolymers [41]. For copolymers of components having different densities, the density and, consequently, also partial specific volume of the copolymer in a solvent varies with its composition. In a density gradient in the cell of an ultracentrifuge, molecules of such a copolymer sediment or float until they reach the layer of the solvent system where the specific volume of the solvent and the partial specific volume of the molecule match. The motion of the molecule, except for Brownian motion, stops in that layer. Thus, a chemically heterogeneous copolymer separates in a density gradient according to the partial specific volume, which is a function of composition. The method is demanding on equipment and performance, and nowadays is used only in special cases.

As a result of the vigorous development of chromatographic techniques with their potential of automation, reduction of the necessary amount of sample, multiple detection, *etc.*, high-performance liquid chromatography (HPLC) and size-exclusion chromatography (SEC) became at present the most widely used techniques for the characterization of chemically heterogeneous copolymers [42].

For a particular copolymer, an elution solvent system can often be found in which the effect of molecular weight is completely eliminated and elution takes place exclusively with respect to chemical composition [43]. Thus, in favorable cases, HPLC yields the distribution function of chemical composition, $w(x)$ [14, 15, 44]. It is worth mentioning that the experimentally determined distributions were, within the limits of relatively large experimental error, in fair agreement with those calculated from the conditions of polymerization.

Hydrodynamic volume of linear copolymer molecules is a function of both molecular weight and chemical composition. Although no systematic study on the effect of chemical composition of copolymer molecules on their hydrodynamic volume seems to exist, model calculations [45] and experimental results [7] indicate that the effect of molecular weight predominates. Thus, depending on the copolymer, better or poorer approximations to the MWD, $w(M)$, are obtained by SEC, separating according to hydrodynamic volume.

The combination of the two chromatographic techniques is apparently the most promising, though not universal, approach to the characterization of chemically heterogeneous copolymers. For several copolymers, it has been demonstrated that, *e.g.*, refractionation by SEC of HPLC fractions, fairly uniform in chemical composition, enabled the two-dimensional distribution, $w(M, x)$, to be constructed [46, 47].

SEC WITH CONCENTRATION AND COMPOSITION DETECTION

SEC with a concentration and a composition detector has frequently been used for characterization of copolymers [48, 49 and refs. cited therein]. Occasionally, the interpretation of results was not unobjectionable and a word of caution may be appropriate. Often, the composition of the eluted copolymer does not change with the elution volume and many authors take this as a proof of chemical homogeneity of the copolymer. Such a result, however, does not permit an unambiguous interpretation. The copolymer may really be chemically homogeneous. The other possibility, however, is that the copolymer is heterogeneous, even appreciably so, but there is no interdependence of molecular weight and chemical composition or, in other words, all fractions more or less uniform with respect to molecular weight have the same distribution in chemical composition and their average composition, recorded by the composition detector, does not change with elution volume.

A change in the composition of the copolymer with elution volume proves that the copolymer is chemically heterogeneous and shows interdependence of molecular weight and chemical composition. The range of compositions observed is a lower limit of the extent of heterogeneity because the fractions eluted at any elution volume have a distribution in chemical composition, *i.e.*, comprise molecules with compositions differing in either direction from the average composition signalled by the detector. An attempt to transform the data into a distribution function of chemical composition is likely to yield an erroneously narrow distribution.

SEC WITH CONCENTRATION AND LIGHT-SCATTERING DETECTORS

The advantage of using in SEC measurements a concentration and light-scattering detector on line is that, for homopolymers and, after application of relevant corrections, for copolymers weight-average molecular weight is measured at all elution volumes and no calibration is required [39].

When using this scheme in the characterization of copolymers, two crucial questions emerge. First, for linear copolymers, the hydrodynamic volume of molecules is a function not only of molecular weight but also of chemical composition. There is no systematic study of the dependence of hydrodynamic volume of copolymer molecules on chemical composition but, in principle, one must expect that, in a SEC measurement on a chemically heterogeneous copolymer, a spectrum of molecules with various combinations of molecular weights and compositions will elute simultaneously. It is important to examine the effect the non-uniformity of the eluted fractions exerts on the result.

The other puzzling question is evoked by the fact that

a light-scattering measurement on a solution of a chemically heterogeneous copolymer, the parent homopolymers of which differ in refractive index and using just one solvent, does not yield its true weight-average molecular weight but only an apparent molecular weight. The difference between the true and the apparent value is the larger, the broader is the distribution in chemical composition and the more differ the refractive indices of the parent homopolymers. Again, a query presents itself: is the difference between the true and the apparent molecular weight significant in typical measurements?

A systematic experimental investigation of the two above questions would require an enormous effort. Extensive model calculations with realistic values of relevant parameters have shown [45]: (*i*) in a chemically heterogeneous copolymer, molecular weights of molecules having the same hydrodynamic volume differ typically by 20—30% depending on their composition; (*ii*) in SEC separation, the effect of molecular weight largely predominates over that of chemical composition and SEC measurements on chemically heterogeneous copolymers yield good approximations to distribution functions of molecular weight even for copolymers with very broad distributions of chemical composition; (*iii*) for virtually all copolymers encountered in routine characterization practice, the difference between the true weight-average molecular weight and the apparent molecular weight calculated from the intensity of scattered light is within the limits of experimental error and the molecular weight values are credible.

CALCULATION OF DISTRIBUTION FUNCTIONS OF CHEMICALLY HETEROGENEOUS COPOLYMERS FROM CONDITIONS OF SYNTHESIS

A number of procedures have been developed to the calculate distribution functions $w(M,x)$, $w(M)$, and $w(x)$ from the conditions of synthesis for chemically heterogeneous copolymers of various types, such as statistical [50—52], block [16], or graft [14, 53] copolymers. When the copolymer was amenable to both calculation of the distribution function of chemical composition and its experimental determination, the two results were in reasonable agreement [54]. Experimental determination of the distribution function of chemical composition of a copolymer is not always feasible. Even if feasible, it is likely to be laborious and not very accurate. Making use of an appropriate computation procedure, if available, is likely to yield a satisfactory result with much less effort.

REFERENCES

[1] Stejskal J., Kratochvíl P.: *Macromolecules 1978*, **11**, 1097. [2] Stejskal J., Kratochvíl P., Straková D.: *Macromolecules* 1981, **14**, 150. [3] Stejskal J., Horská J., Kratochvíl P.: *Macromolecules 1984*, **17**, 920. [4] Stejskal J., Kratochvíl P.: *Makromol. Chem.* 1987, **188**, 2435. [5] Myagchenkov V. A., Frenkel S. Y.: „Compositional Heterogeneity of Copolymers" (in Russian), Khimiya, Leningrad 1988. [6] Podešva J., Stejskal J., Procházka O., Špaček P., Enders S.: *J. Appl. Polym. Sci.* 1993, **48**, 1127. [7] Montaudo M. S., Montaudo G.: *Macromolecules* 1999, **32**, 7015. [8] Stejskal J., Kratochvíl P.: *J. Appl. Polym. Sci.* 1980, **25**, 407. [9] Stockmayer W. H.: *J. Chem. Phys.* 1945, **13**, 199. [10] Cheng H. N.: *Int. J. Polym. Anal. Character.* 1997, **4**, 71.

[11] Stejskal J., Kratochvíl P.: *J. Appl. Polym. Sci.* 1978, **22**, 2925. [12] Schoonbrood H. A. S., Thijssen H. A., Brouns H. M. G., Peters M., German A. L.: *J. Appl. Polym. Sci.* 1993, **49**, 2029. [13] Stejskal J., Straková D., Kratochvíl P., Smith S. D., McGrath J. E.: *Macromolecules* 1989, **22**, 861. [14] Kawai T., Teramachi S., Tanaka S., Meada S.: *Int. J. Polym. Anal. Charact.* 2000, **5**, 381. [15] Teramachi S., Sato S., Shimura H., Watanabe S., Tsukahara Y.: *Macromolecules* 1995, **28**, 6183. [16] Stejskal J., Kratochvíl P.: *Polym. J.* 1982, **14**, 603. [17] Benoît H., Marot G., Panaras R., Perrinaud R.: *J. Appl. Polym. Sci.* 1996, **62**, 1847. [18] Pallaske U., Kuhn R.: *Makromol. Chem.* 1986, **187**, 1777. [19] Knyazeva T. E., Myasnikova I. B., Semchikov Y. D.: *Vysokomol. Soedin. A* 1998, **40**, 1360. [20] Elbegawy S. E. M., Huglin M. B.: *Polym. J.* 1993, **25**, 435.

[21] Braun D., Meyer M. I.: *Macromol. Chem. Phys.* 1998, **199**, 735. [22] Stejskal J., Kratochvíl P., Hrouz J.: *Colloid Polym. Sci.* 1979, **257**, 931. [23] Listvoib G. I., Raigorodskii I. M., Goldberg E. S., Kireev V. V., Tsivinskaya L. K.: *Vysokomol. Soedin. A* 1991, **33**, 778. [24] Feng Y. D., Hay J. N.: *Polymer* 1998, **39**, 6723. [25] Feng Y. D., Hay J. N.: *Polymer* 1998, **39**, 6589. [26] Feng Y. D., Jin X. R., Hay J. N.: *Polym. J.* 1998, **30**, 215. [27] Feng Y. D., Jin X. R., Hay J. N.: *J. Appl. Polym. Sci.* 1998, **68**, 395. [28] Gattiglia E. G., Turturro A., Tonelli C., Trombetta T., Ajroldi G.: *Int. J. Polym. Anal. Character. 1998*, **4**, 295. [29] Ma D. Z., Wang M. T., Wang M. Z., Zhang X. Y., Luo X. L.: *J. Appl. Polym. Sci.* 1998, **69**, 947. [30] Schulz G. O., Milkovich R.: *Polym. Int.* 1994, **33**, 141.

[31] Markel E. J., Weng W., Peacock A. J., Dekmezian A. H.: *Macromolecules* 2000, **33**, 8541. [32] Stejskal J., Kratochvíl P.: *Macromolecules* 1978, **11**, 1097. [33] Kuhn R.: *Makromol. Chem.* 1980, **181**, 1986. [34] Fonseca C. A., Harrison I. R.: [in:] „Modern Techniques for Polymer Characterisation" (*Eds.*, Pethrick R. A., Dawkins J. V.), Wiley, Chichester 1999; p 1—13. [35] Soares J. B. P., Hamielec A. E.: [in:] „Modern Techniques for Polymer Characterisation" (*Eds.*, Pethrick R. A., Dawkins J. V.), Wiley, Chichester 1999; p. 15—55. [36] Xu J. T., Feng L. X.: *Eur. Polym. J.* 2000, **36**, 867. [37] Soares J. B. P., Hamielec A. E.: *Macromol. Theory Simul.* 1995, **4**, 305. [38] Stejskal J., Kratochvíl P., Straková D., Procházka O.: *Macromolecules* 1986, **19**, 1575. [39] Kratochvíl P.: „Classical

Light Scattering from Polymer Solutions", Polymer Science Library 5 (Ed., Jenkins A. D.), Elsevier, Amsterdam 1987. [40] Podešva J., Stejskal J., Kratochvíl P.: Macromolecules 1987, 20, 2195.

[41] Stacy C. J.: J. Appl. Polym. Sci. 1977, 21, 2231. [42] Balke S. T. [in:] „Modern Methods of Polymer Characterization" (Eds., Barth H. G., Mays J. W.), Wiley, New York 1991; p 1—66. [43] Braun D., Kramer I., Pasch H., Mori S.: Macromol. Chem. Phys. 1999, 200, 949. [44] Fedorov E. K., Kedik C. A.: Vysokomol. Soedin. A 1994, 36, 1548. [45] Netopilík M., Bohdanecký M., Kratochvíl P.: Macromolecules 1996, 29, 6023. [46] Glöckner G, Stejskal J., Kratochvíl P.: Makromol. Chem. 1989, 190, 427. [47] Glöckner G., Stickler M., Wunderlich W.: J. Appl. Polym. Sci. 1989, 37, 3174. [48] Mori S., Suzuki T.: J. Liq. Chromatogr. 1981, 4, 1685. [49] Pasch H.: Adv. Polym. Sci. 2000, 150, 1. [50] Galbraight M. N., Moad G., Solomon D. H., Spurling T. H.: Macromolecules 1987, 20, 675.

[51] Cheng H. N.: Macromolecules 1992, 25, 2351. [52] Cheng H. N., Tam S. B., Kasehagen L. J.: Macromolecules 1992, 25, 3779. [53] Stejskal J., Kratochvíl P., Jenkins A. D.: Macromolecules 1987, 20, 181. [54] van Doremaele G. H. J., Geerts F. H. J. M., aan de Meulen L. J., German A. L.: Polymer 1992, 33, 1512.

❄ ❄ ❄ ❄ ❄ ❄ ❄ ❄ ❄

Najlepsze życzenia szczęśliwego
Nowego Roku 2002
Czytelnikom, Autorom i Współpracownikom

składa
Redakcja

❄ ❄ ❄ ❄ ❄ ❄ ❄ ❄ ❄ ❄