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The Use of Lanthanide Shift Reagents in the Analysis of the Micro-structure of Polymers by NMR Spectroscopy

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The principal results obtained by using lanthanide shift reagents (LSR) to analyse the micro-structure of polymer chains by ^{1}H and ^{13}C NMR spectroscopy have been examined. A short theoretical introduction to the LSR method has been given, and the magnetic properties of the lanthanides have been examined from the viewpoint of their possible use as LSR. Particular attention has been paid to the solution of the main problems in the structural analysis of polymer chains: the determination of stereoregularity and the nature of the alternation of the monomer units along a copolymer chain, and the investigation of the distribution of *cis*- and *trans*-units and the conformational mobility of homopolymer chains with and without polar groups. The bibliography contains 57 references.

CONTENTS

I. Introduction. The micro-structure of polymers 817
II. Lanthanide shift reagents in NMR spectroscopy. Theory of the method 817
III. The use of shift reagents to analyse the micro-structure of a polymer chain 819

I. INTRODUCTION. THE MICRO-STRUCTURE OF POLYMERS

The physicochemical properties of a polymer are determined chiefly by the structure of the repeat unit of the chain, but there are practically no ideal regular chains. Real polymers contain the most varied chain structural defects, which can produce significant changes in the properties of the polymer. Information on the distribution of defect units of different types along the chain provides a quantitative reflection of the micro-structure of the polymer.

High-resolution NMR now occupies a dominant position in the study of the micro-structure of polymer chains.[1-4] Because of the marked dependence of the electronic shielding of the nuclei on the chemical environment, the displacement of the signals in the NMR spectra takes place as a consequence of not only the alternation of chemically different monomer units but also the alternation of the relative configurations of successive identical monomer units containing pseudo-asymmetric carbon atoms. This makes it possible to use NMR spectroscopy to solve three types of problem: 1) the composition analysis of the distribution of monomer units along the chain, including the determination of the type of orientational connection "head to head", "head to tail", and "tail to tail"; 2) measurement of the degree of stereoregularity of the chain; and 3) conformational analysis, including the study of phase transformations (of the globule–coil type).

Experimental approaches to the analysis of the micro-structure of the chain are associated with the measurement of the relative concentration of different fragments and the sequence of monomer units from the integral intensities of their signals in the NMR spectrum. The maximum length of this fragment which can be identified by NMR at present does not exceed 8–9 monomer units.[5] Thus the experimental data describe directly the distribution of the units only in short sections of the chain. To analyse the distribution of the units along the entire chain of the macromolecule, it is necessary to assume that the processes controlling the growth of the chain during polymerisation are random in character and are described by Bernoulli or Markov statistics of first and second orders.[4]

The information provided by the NMR spectra of polymers (particularly ^{1}H NMR) is decreased, however, by the fact that the nuclei of aliphatic groups around which there are no electronegative atoms give signals with similar chemical shift values. Moreover, there are a whole range of fundamental physical factors[5] leading to broadening and overlap of the NMR signals from different structural sequences of the polymer chains. Thus the number of polymers which can be readily analysed is small, and to investigate the micro-structure of polymers it is usually necessary to use either shift reagents or NMR spectrometers with a superconducting magnet, or a combination of these methods.

II. LANTHANIDE SHIFT REAGENTS IN NMR SPECTROSCOPY. THEORY OF THE METHOD

The influence of paramagnetism on the characteristics of nuclear resonance was detected by Bloembergen and Dickinson.[6] The characteristic features of NMR in paramagnetic systems have been examined in detail in a large number of theoretical and experimental studies[7-10] and summarised in a number of reviews and monographs.[11-15]

The paramagnetic centres include lanthanide cations having an unpaired electron. The interaction between the unpaired electron and the nucleus whose magnetic resonance is being observed is revealed by an isotropic hyperfine shift of the signal,[7] a change in the nuclear relaxation times T_1 and T_2, and in the nuclear polarisation of the spins as a result of the Overhauser effect.[8] These changes give information on the electronic and geometric structure of the ligands joined to the paramagnetic centres.

1. The Paramagnetic Shift

The isotropic shift of the signals in the NMR spectra of paramagnetic substances is determined by the sum of two types of interaction: contact and pseudocontact.

A Fermi contact shift takes place if the spin density of the unpaired electron is delocalised and is transferred through a system of chemical bonds to the nucleus whose resonance is being observed. A contact shift obeys the Curie law and in the case of a one-spin state with an isotropic g-tensor is described by the equation:[6]

$$\frac{\Delta H}{H_0} = -\frac{Ag^2\beta^2}{g_N\beta_N}\cdot\frac{s(s+1)}{3kT}$$

where A is the hyperfine interaction constant, g_N the nuclear g-factor, β_N the nuclear magneton, H_0 the intensity of the external magnetic field, β the Bohr magneton, g the Landé

factor, k the Boltzmann constant, T the absolute temperature, and s the spin quantum number of the electron.

The contact shift of a signal is observed with the condition that $T_{1e}^{-1} \gg A$, where T_{1e} is the electronic spin–lattice relaxation time. Contact shifts are large for oxygen and nitrogen nuclei coordinated directly to the paramagnetic centre, and also for carbon chemically combined with these atoms. For more distant atoms, including all protons, the contact shifts are small, and the paramagnetic shifts observed in the NMR spectra have pseudocontact character.[11-15]

The pseudocontact shift is determined by the dipole–dipole interaction of the spins of the unpaired electron and the nucleus whose resonance is being observed; its magnitude depends on the electron configuration of the paramagnetic ion, the degree of magnetic anisotropy of the ligand field, and temperature.

The magnitude of the pseudocontact shift of a signal is inversely proportional to the cube of the distance from the paramagnetic centre to the nucleus being observed, and depends on angular factors. For axial symmetry of the complex, the pseudocontact shift is determined[7] by the McConnell–Robertson equation:

$$\frac{\Delta H}{H_0} = -\frac{\beta^2 s(s+1)}{9kT}(g_{\parallel}^2 - g_{\perp}^2)\frac{3\cos^2\theta - 1}{r^3} \qquad (2)$$

where $g_{\parallel}$ and $g_{\perp}$ are the components of the g-tensor of the magnetic anisotropy in directions parallel to and perpendicular to the principal axis of the complex, r the distance to the nucleus, and θ the angle between the radius vector $\boldsymbol{r}$ and the principal axis of the complex.

The dependence of the pseudocontact shift on the geometry of the complex,[7] described by Eqn.(2), makes it possible to assign the signals in the spectrum of a ligand with known structure or to solve the inverse problem, that is from the known assignment to obtain information on the geometry of a molecule.[10-16]

2. Paramagnetic Broadening

In the presence of a paramagnetic centre, broadening of the NMR signals is observed, due to the acceleration of the relaxation of the nuclear spin and the influence of exchange by molecules of the substrate between bound and free states. The main factor determining the width of the NMR signals of the substrate is the electronic spin–lattice relaxation time of the paramagnetic ion T_{1e}. For the complexes of ions with small values of $T_{1e} \ll \hbar/Ag\beta$ (Eu^{3+}, Pr^{3+}, Nd^{3+}), slight broadening is observed. Ions with large $T_{1e} \gg \hbar/Ag\beta$ (Gd^{3+}, d elements such as Mn^{2+}) give extensive broadening.[14]

The spin–lattice T_1 and spin–spin T_2 relaxation times for nuclei with spin 1/2 in the presence of a paramagnetic centre are determined by the Solomon–Bloembergen equations.[8] The first terms of these equations are due to dipole–dipole interaction, and depend on the distance r between the nucleus being observed and the paramagnetic centre. This interaction is determined by the correlation time of the dipole electron–nucleus interaction τ_c. The second terms, which do not depend on r, are characterised by the correlation time of the contact interaction τ_e. The relaxation times are influenced only by variable effects whose correlation times are of the same order of magnitude as the period of the Larmor precession of the nuclear spins.

The correlation times are determined by the expressions

$$\tau_c^{-1} = \tau_R^{-1} + \tau_S^{-1} + \tau_M^{-1} + \tau_D^{-1} \qquad (3)$$

$$\tau_e^{-1} = \tau_S^{-1} + \tau_M^{-1} \qquad (4)$$

where τ_R, τ_S, τ_M, and τ_D are the correlation times corresponding to rotational motion, relaxation of the electron spin, and chemical and diffusion exchange respectively.

3. The Magnetic Properties of the Lanthanides and Their Use as Shift Reagents

Lanthanides have short electronic spin relaxation times $\tau_S \cong 10^{-12}$–10^{-13} s at 300 K. Exceptions are provided by ions with the $4f^7$ electron configuration (Gd^{3+}, Eu^{3+}), which have long times τ_S ($\tau_S \cong 10^{-10}$ s for Gd^{3+}). The unique position of Gd^{3+} among the lanthanides is related to the fact that its ground state is $^8S_{7/2}$, $L = 0$, and the magnitude of the angular momentum is determined entirely by the spin. This state does not interact with an electric field, so that the rate of relaxation of the electron spin decreases.

Thus the lanthanides, except Gd^{3+} and Eu^{3+}, should have little influence on the magnetic resonance line width, if chemical exchange is sufficiently rapid, and they can be used as shift reagents. Gadolinium, like the ions of d elements, is a relaxation (broadening) reagent. The action of Eu^{3+} as a shift reagent is due to the displacement of the ground and excited states.

The theoretical calculation of the magnitude of pseudocontact shifts brought about by the lanthanides has been described.[9]

The correct interpretation of the data obtained using lanthanide shift reagents (LSR) also gives complete pictures of the structure of compounds in solution, which can only be compared with X-ray diffraction data for determining crystal structures. The LSR most widely used as paramagnetic probes are europium and praseodymium salts and their complexes with 2,2,6,6-tetramethylheptan-3,5-dione (dpm), 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctan-4,6-dione (fod), and d-camphor. The salts are used in polar solvents. In most known cases, europium salts displace the signals towards strong fields, and praseodymium salts towards weak fields.[16] In non-polar solvents, complexes with the above ligands, lanthanide tris(β-diketonates), are used, for example $Eu(fod)_3$, $Pr(dpm)_3$; europium β-diketonates usually displace NMR signals in the spectra of substrates towards weak fields, and praseodymium towards strong fields.[17]

NMR spectra obtained in the presence of LSR are interpreted by two methods. The first involves the qualitative analysis of the spectrum modified using LSR. In the second case the shift values are used to obtain information on the structure of the substrate.

The qualitative interpretation of the spectra does not require assumptions about the nature of the bond between the LSR and the substrate. When the LSR is added, the assignment of the signals in the NMR spectrum of the substrate is simplified because of the difference in the induced shift of the signals from different nuclei. It follows from Eqn.(2) that a greater shift is undergone by the signals of nuclei situated closer to the coordination centre of the substrate molecule.

To obtain information on the structure of a substrate from Eqn.(2), it is necessary to have a large amount of data on the structure of the complex. Some of these data can be obtained by X-ray diffraction and from luminescence spectra.[15] This does not however eliminate the difficulties associated with the need to separate from the induced total paramagnetic shift of the signal the pseudo-component, which is determined by the geometry of the substrate.[17]

All methods for separating the contributions of contact and pseudocontact shifts are based on the difference in the dependence of their magnitude on the atomic number of the

lanthanide. The behaviour of the signals in the presence of europium and gadolinium is most informative for investigating the question of the existence of contact shifts in a given system.[12,16] If a shift is detected in the presence of gadolinium, this indicates the existence of a contact shift of the signal from the nucleus of the substrate being considered, since the pseudocontact shift induced by gadolinium is zero. By measuring the displacement of the signals from the same nuclei in the presence of different lanthanides, it is possible to obtain a system of linear equations which make it possible to determine quantitatively the contact and pseudocontact contributions to the induced shifts.[12,15] An unsatisfactory feature of all existing methods of separation is the need to make an assumption about the axial symmetry of the complex.[15]

III. THE USE OF LANTHANIDE SHIFT REAGENTS TO ANALYSE THE MICRO-STRUCTURE OF A POLYMER CHAIN

1. The Separation of Signals from Stereosequences

The first applications of LSR to study a number of polymers with functional groups were aimed merely at simplifying the form of the NMR spectra.[18-29] The addition of $Eu(dpm)_3$, $Eu(fod)_3$, and $Pr(fod)_3$ improved the resolution of the signals in the spectra of polymethyl methacrylate (PMMA), polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl acetate, polypropylene oxide, polysiloxane,[18,19] polyesters,[20,21] polyols,[22-26] polylacetones,[27,28] polypeptides,[29] and other polymers.

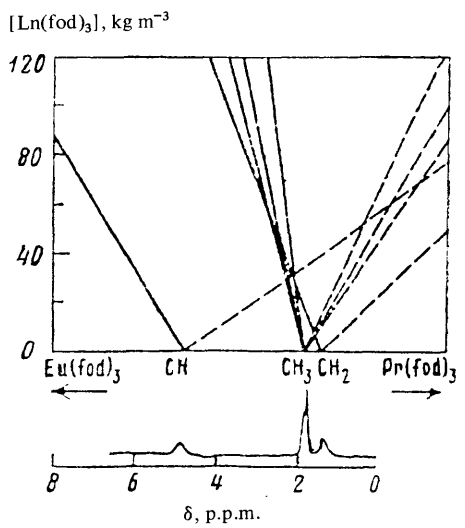


Figure 1. Influence of the concentration of $Eu(fod)_3$ (continuous lines) and $Pr(fod)_3$ (broken lines) on the ^1H NMR spectrum of polyvinyl acetate solution.[18]

Guillet and co-workers[19] were the first to discover that the shifts of the triad signals from the methyl and methoxycarbonyl groups of PMMA in o-dichlorobenzene decrease in the following order when an LSR is added (*i*-, *h*-, and *s*- denotes iso-, hetero-, and syndiotactic triads): $s\text{-}CCH_3 > i\text{-}CCH_3 > h\text{-}CCH_3 > i\text{-}OCH_3 > s\text{-}OCH_3 > h\text{-}OCH_3$. The order of change in the shifts is different in benzene: $i\text{-}CCH_3 > h\text{-}CCH_3 > s\text{-}CCH_3 > i\text{-}OCH_3 > h\text{-}OCH_3 > s\text{-}OCH_3$. This difference reflects the dependence of the conformation of the polymer on the micro-tacticity.[18-20]

Fig.1 shows the ^1H NMR spectrum of polyvinyl acetate in $CDCl_3$ and the influence of the addition of small quantities of $Eu(fod)_3$ and $Pr(fod)_3$ to the solution.[18] Both reagents separate the signal from the methoxycarbonyl proton into iso-, hetero-, and syndiotactic triads. The slopes of the straight lines on the diagram characterise the relative magnitude of the induced shift. $Pr(fod)_3$ produces larger shifts than $Eu(fod)_3$, and slightly greater paramagnetic broadening.

The determination of the micro-tacticity of poly-β-substituted β-propiolactones is a fundamental problem in the study of stereoregulation. A promising route to its solution has appeared with the use of $Eu(dpm)_3$ to separate the signals from meso (*m*) and racemic (*r*) diads in the ^{13}C NMR spectra.[27] The stereospecificity of induced paramagnetic shifts is due to the difference of 1–4° in the values of the angles θ in Eqn.(2) for the neighbouring carbon atoms of ^{13}CO and $^{13}CH_2$ in the *m* and *r* configurations of the polymer chain as a consequence of the restricted rotation relative to the bond joining these atoms.

The influence of $Eu(dpm)_3$ and $Dy(fod)_3$ on the ^{15}N NMR spectra of polypeptides has been studied.[29] The spectra of Z–Glu–Leu–*Leu–OMe (Fig.2) show that the addition of $Dy(fod)_3$ produces a selective shift of the ^{15}NH signals from different aminoacids. This is due to the difference in the chemical and spatial environments of the nitrogen atoms.

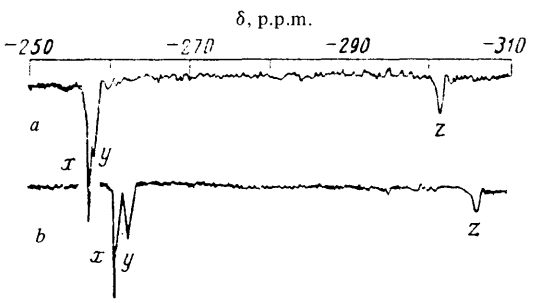


Figure 2. ^{15}N $\{^1H\}$ NMR spectra of a solution of Z–Glu–Leu–*Leu–OMe in CH_2Cl_2 before (*a*) and after (*b*) the addition of $Dy(fod)_3$ in the ratio N/Dy = 60 : 1. The chemical shifts are measured from the signal of $^{15}NO_3$ [29] (*x*—*Leu, *y*—Leu, *z*—Glu).[29]

The paramagnetic shift values depend on the distribution of the europium ions between different coordination centres in polyethylene glycol and polyformaldehyde chains.[22] It should be noted, however, that few authors take account of this distribution, which is capable of influencing the interpretation of the spectra considerably, particularly in the determination of the transformation of the polymer chain.

2. The Conformational Mobility of Homopolymer Chains

All approaches to the examination of the conformation of polymer chains are based on the use of some form of the McConnell–Robertson equation (2) after separation of the

contact and pseudocontact contributions to the induced paramagnetic shift. It is therefore of interest to examine the stereospecific contact interaction in the NMR spectra of polyol–lanthanide complexes (La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}, Yb^{3+}).[26] If the chain has a planar zigzag conformation, the main contribution to the paramagnetic shift is made by contact interaction. In other cases, the isotropic shift of the signal is predominantly pseudocontact. This was used[30] to establish the possible conformations of iso- and syndiotactic PMMA in solution by comparing the observed values of the pseudocontact shift with the values of the geometric factor $(1-3\cos^2\theta)/r^3$ in Eqn.(2), calculated for all planar or spiral conformations of the chain.

Fig.3 gives the dependence of the values of the induced paramagnetic shifts $\Delta\delta$ of the signals from the protons of three groups (α-CH_3, CH_2, and OCH_3) for iso- and syndiotactic PMMA in solutions in $CDCl_3$ and C_6D_6 on the $Eu(dpm)_3$ concentration. The values of $\Delta\delta$ depend on the distance of the protons from the coordination site, and for syndiotactic PMMA also on the nature of the solvent.

In spite of the fact that a flexible polymer chain cannot have a fixed conformation in solution,[4] it has been shown that isotactic PMMA exists in a right-hand spiral (10/1) conformation. The *trans*-zigzag conformation established for syndiotactic PMMA is a unique case of planar or spiral conformation.

The influence of the shift reagents $Eu(dpm)_3$ and $Pr(dpm)_3$ on the ^1H NMR spectra of a solution of atactic poly-4-vinylpyridine (P-4-VP) in $CDCl_3$ has been studied in the temperature range 28–100 °C.[31] The micro-structure of radical P-4-VP, determined from the ^1H and ^{13}C spectra, corresponds effectively to Bernoulli statistics with $P_m = 0.52$. The shifts of the proton signals in the spectra of the polymer, induced by adding $Eu(dpm)_3$, are due to pseudocontact interaction. The values of the geometric factor were calculated for fragments of the macromolecule with regular iso- or syndiotactic-sequences. The conformations of the polymer were determined from the maximum probability of agreement between the experimental and calculated values of the induced shifts. The concentrations of the structures $[2_1]$ = 47 mole % (TTGG), $[Z_S]$ = 28 mole % (*trans*-zigzag), and $[3_1]$ = 25 mole % (isotactic) agree with the proposed model of the micro-tacticity of P-4-VP. The temperature dependence of the shifts of the ^1H signals indicated a change in the ratio of the conformations of P-4-VP towards an increase in the concentration of the syndio-*trans*-form.

$Eu(fod)_3$ was used similarly to determine the concentration of the TGT conformation of the sequence COCCOC in polyethylene glycol.[25] When europium is added to the polymer solution, the NMR signals assigned to the ethylene protons in the polymer segments separate into four groups of signals from the ethylene protons, close to the end of the chain, and a singlet in a weak field from TGT. The concentration of the TGT form increases rapidly with increase in the number-average molecular mass of the polymer.

3. Analysis of the Nature of the Alternation of Monomer Units Along the Polymer Chain

The use of LSR makes it possible to obtain extensive information on the distribution of the monomer units along copolymer chains, not obtainable by other methods of physicochemical analysis.[32] A necessary condition for the applicability of shift reagents to the analysis of the micro-structure of copolymers, as in the case of homopolymers, is the presence of atoms with an unshared pair of electrons (nitrogen or oxygen) in the main or side chains. The copolymers studied with a nitrogen atom in the side chain include copolymers of acrylonitrile with 1,3-dialkenes,[33–37] and with an oxygen atom, the copolymers of methyl methacrylate (MMA)[38–40] and α,β-unsaturated ketones with 1,3-dialkenes,[41–43] of methyl methacrylate with styrene,[44] and of ethylene with vinyl acetate.[45] In spite of the complexity of the interpretation of the spectra, the LSR method has been applied successfully to copolycondensed polymers containing an oxygen atom in the main chain.[46,49]

The application of the LSR method to copolymers containing a hetero-atom in the side chain is based on the fact that the signals of the triads having a large number of coordination centres, for example CN or CO, and hence a large number of polar (P) monomer units undergo a larger induced lanthanide shift than triads containing chiefly non-polar (N) units. The magnitude of the induced paramagnetic shift of the signals from the triads increases in the series NPN < NPP < PPP, NNN ≪ NNP < PNP.[32–34] This was used to assign the signals in the spectra, and the results agreed well with the results obtained by ^{13}C NMR spectroscopy[47] and with existing statistical theories describing the nature of the growth of the polymer chain.[37–42]

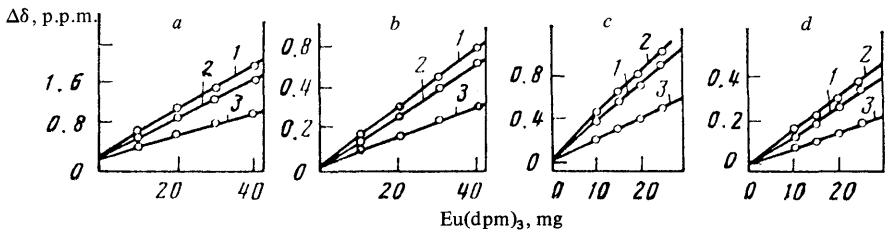


Figure 3. Dependence of the induced paramagnetic shift of the signals of CH_2 (*1*), CH_3 (*2*), and OCH_3 (*3*) on the quantity of $Eu(fod)_3$ for iso- (*a*,*c*) and syndiotactic (*b*,*d*) PMMA at 25 °C (*a*,*b*) and 80 °C (*c*,*d*) in $CDCl_3$.[30]

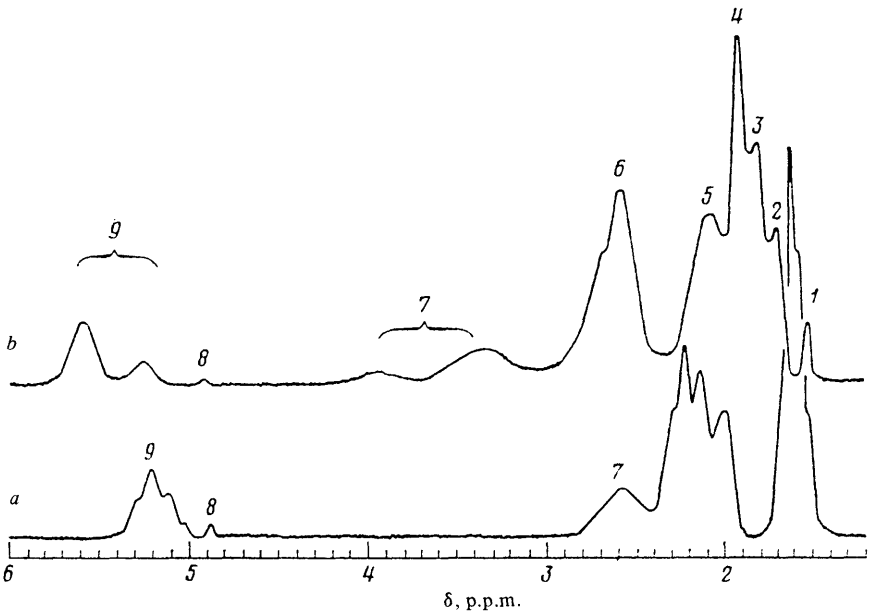


Figure 4. ^{1}H NMR spectra of a solution of the copolymer of isoprene (I) and acrylonitrile (A) (51.2 mole % A) in $CDCl_3$: *a*) without the addition of Eu(fod)$_3$, *b*) after the addition of Eu(fod)$_3$ at a mass ratio Eu(fod)$_3$:copolymer of 1:1. Assignment of the signals: *1*) CH_3-III; *2*) CH_3-AII, CH_2-III; *3*) CH_2-IAI; *4*) CH_3-AIA; *5*) CH_2-AII; *6*) CH_2-AIA + AAI + AAA; *7*) CH–CN; *8*) 1,2-I; *9*) =CH-III + AII + AIA.[35]

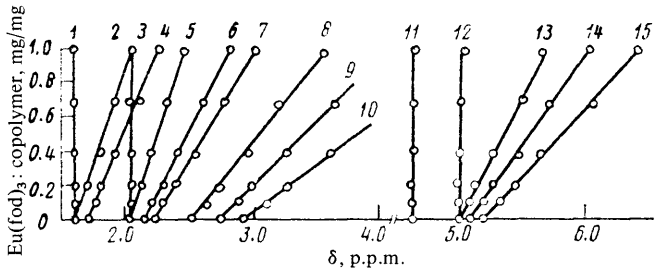


Figure 5. Dependence of the magnitude of the induced paramagnetic shift of the ^{1}H NMR signals of the triad and tetrads in the spectrum of the copolymer of isoprene with acrylonitrile (40 mole % A) on the mass ratio Eu(fod)$_3$: copolymer. CH_3: *1*) III, *2*) IIA; CH_2: *3*) IIA, *4*) IAI, *5*) IAAI, *6*) IAAA, *7*) AAAA; CH, A: *8*) IAI, *9*) IAA, *10*) AAA, *11*) 1,2-I; $=CH_2$, =CH: *12*) III, *13*) AII, *14*) AIA, *15*) AAIA.[36]

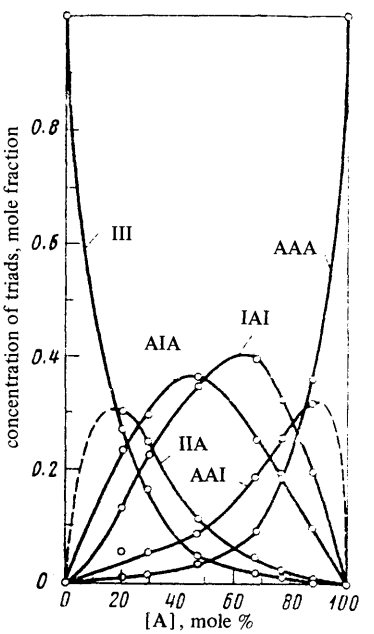


Figure 6. Dependence of the triad composition of copolymers in the mass of isoprene with acrylonitrile on the acrylonitrile concentration.[32]

Fig.4 gives the ^{1}H NMR spectra of the copolymer of isoprene (I) with acetonitrile (A) before and after the addition of Eu(fod)$_3$. Fig.4*b* shows that after the addition of Eu(fod)$_3$ to the copolymer solution, the signals from different triads containing acetonitrile units are separated and displaced to weaker fields. Fig.5 gives the dependence of the magnitude of the induced paramagnetic shift on the ration Eu(fod)$_3$:copolymer for the signals of the copolymer of isoprene with acetonitrile. The magnitude of the induced shift of the signals increases in the series IAI < IAA < AAA; III ≪ IIA < AIA; CH_3 < CH_2-I ≤ =CH < CH_2-A < CHCN.[36,37] The last series proves that the nitrogen of the nitro-group [cyano group, (Ed. of Translation)] is coordinated to europium.

The values of the integral intensities of the signals from different triads give information on the micro-structure, and make it possible to find the statistics of the distribution of

the monomer units along the chain. Fig.6 gives the dependence of the triad composition of the copolymers of isoprene with acetonitrile, obtained by copolymerisation in the mass, on the acetonitrile concentration [A]. The asymmetry of the arrangement of the maxima on the curves indicates that the nature of the growth of the copolymer chain does not correspond to Bernoulii statistics and that there are mutually opposed tendencies in the formation of the chain by the monomer units: isoprene tends to undergo homopolymerisation, and acetonitrile to undergo heteropolymerisation.[33]

The micro-structure of industrial SKN-18, -26, -40 butadiene–nitrile rubbers with different acetonitrile concentrations was studied analogously.[34] The absence of shift, induced by the addition of $Eu(fod)_3$, of the signal from the 1,2-structures of butadiene and separation into its components made it impossible to reach conclusions about the isolation of the 1,2-structures within the butadiene micro-blocks.

The micro-structure of copolymers of MMA with 1,3-dialkenes has been analysed using a shift reagent.[38–40] $Pr(fod)_3$ was used to determine the micro-structure of copolymers of MMA with isoprene.[38] The growth of the chains of the copolymers obtained in the mass obeys first-order Markov statistics with copolymerisation constants $r_{MMA} = 0.26$ and $r_I = 0.625$.

First-order Markov statistics also describe the copolymer of chlorophene with MMA, since the concentration in it of the pentad with an MMA unit at the centre, determined from the splitting of the methoxyl signal when $Eu(dpm)_3$ is added, agrees with that calculated from the copolymerisation constants.[39]

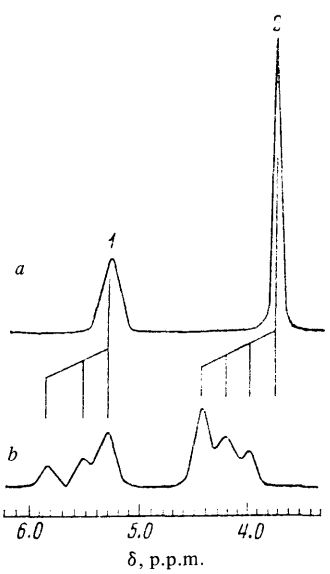


Figure 7. ^1H NMR spectra of a solution of the copolymer of butadiene with MMA in CCl_4: *a*) without the addition of $Eu(fod)_3$, *b*) after the addition of $Eu(fod)_3$; *1*) CH= (MBM, BBM, BBB), *2*) OCH_3 (MMM, MMB, BMB). The signals from the triads were recalculated in the direction of increase in the field.[40]

Fig.7 shows the ranges of the signals from the alkene and methoxyl protons of the copolymer of butadiene (B) with MMA (M).[40] When $Eu(fod)_3$ is added to a solution of the copolymer, these signals are split into the signals from the triad. The magnitude of the induced paramagnetic shift of the signals increases in the series BBB << BBM < MBM; BMB < BMM < MMM; $-CH_2-B <$ =CH– < $-CH_2-M < -OCH_3 < CCH_3$. The values of the induced shifts indicate that the carboxyl and ester oxygen atoms are coordinated to europium.

The information on the micro-structure of copolymers, obtained by NMR spectroscopy using shift reagents, makes it possible to reach conclusions about the mechanism and topochemistry of the copolymerisation. For example, the dependence of the micro-structure of emulsion copolymers of isoprene with acetonitrile and of butadiene with MMA on the stability of the layer of surface-active agent (SAA) on the surface of the polymer–monomer particle has been established.[32,33,35–37,40] Fig.8 clearly shows the relationship between the criterion of the stability of the layer of SAA (the half-width $\Delta\nu_{1/2}$) of the signal from $(CH_2)_n$ in the ^1H NMR spectrum of mixed micelles of sodium alkylsulphonate (SAS) with potassium dresinate (PDR)[48] and the triad composition of the copolymers obtained in these systems.[35,37] The chain growth of the emulsion copolymers of isoprene with acetonitrile is described by first-order Markov statistics.[35]

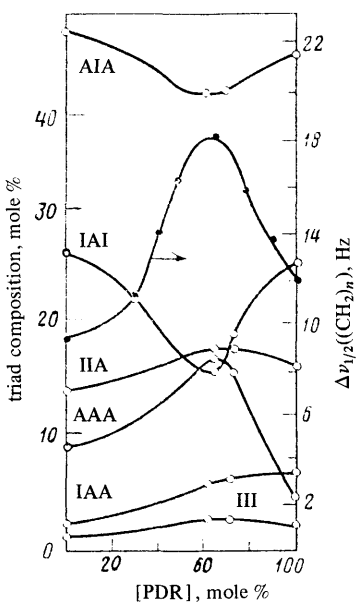


Figure 8. Dependence of the concentration of the triads and $\Delta\nu_{1/2}((CH_2)_n)$ in the ^1H NMR spectra of micelles of SAS and PDR on the PDR concentration.[37]

Analogous results on the influence of the stability of the SAA layer on the micro-structure have been obtained for emulsion copolymers of butadiene with MMA.[40] The SAA used were salts of aliphatic acids, differing in methylene chain length or in the number and position of double bonds, and hence in the stability of the SAA layer on the surface of the polymer–monomer particle. In particular, increase in the length of the methylene chain leads to an increase in the packing density and stability of the SAA layer.[40] Fig.9 shows that the dependence of the concentration of block and alternant triads in the copolymers on the length of the methylene chain is linear. The growth of the chain of the

emulsion copolymers of butadiene with MMA obeys first-order Markov statistics. The results made it possible to distinguish the zones in which homopolymerisation of monomers of different polarity takes place.[35,36,40]

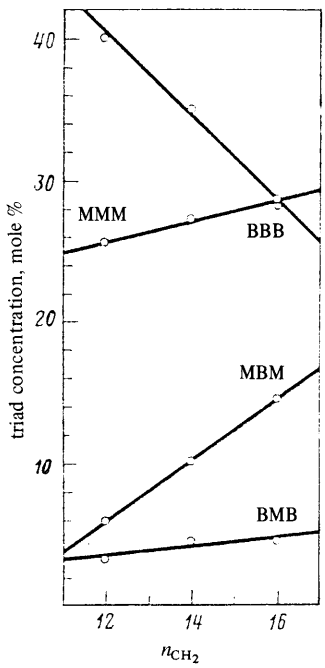


Figure 9. Dependence of the concentration of the triads in the emulsion copolymer of butadiene with MMA on the number of methylene groups in the molecules of the saturated aliphatic acid emulsifiers.[40]

The shift reagent $Eu(fod)_3$ has also been used to analyse the micro-structure of copolymers of α,β-unsaturated ketones (K) with isoprene (I), obtained by radical copolymerisation in the mass and in solution.[41-43] When $Eu(fod)_3$ was added, the signal from the alkene protons was separated into three components, which were assigned to the triads III, IIK, and KIK (listed in the direction of decrease in the field).[41] The experimental values of the concentrations of the triads show good agreement with those calculated from the ^{13}C NMR spectra and from the values of the copolymerisation constants, determined independently (by copolymerisation directly in the NMR spectrometer). The high concentration of the triad KIK confirms the tendency for the copolymers studied to show alternation.[42]

The addition of $Eu(fod)_3$ to a solution of the copolymer of methyl methacrylate with styrene leads to an increase in the resolution in the spectrum of the signals from triad configurations giving a contribution to the signal from the OCH_3 group.[44] The orientation of the LSR molecule in the copolymer chain is determined by the steric influence of the aromatic ring.

The ^1H NMR spectra of copolymers of ethylene with vinyl acetate have been interpreted using $Eu(fod)_3$.[45] The displaced signals from the methine and methyl acetate protons were assigned to the triad sequences of vinyl acetate, and their concentration was compared with that calculated from Bernoulli's model. Comparison of the results showed good agreement.

^1H NMR spectroscopy using $Eu(fod)_3$ and $Pr(fod)_3$ as LSR has been used to analyse the distribution of monomers in the chains of copolyarylates based on dimethyl-bis-phenol, phenolphthalein, and terephthalyl chloride, obtained by high-temperature polycondensation in α-chloronaphthalene.[46] The coefficients of the non-regularity of the copolyarylate chain were determined from the splitting, in the presence of the shift reagent, of the signal at 8.40 p.p.m. from terephthalyl chloride into peaks from the triad. In the copolyarylate synthesised at the isokinetic temperature (200 °C) for the given system, the copolymer units are distributed along the chain according to a random law, whereas in the copolyarylates obtained at other temperatures, copolymer blocks tend to form.

The use of LSR gives a good effect in ^{13}C NMR spectroscopy, as shown by an analysis of the distribution of sequences from the "unreliable", in the sense of the assignment of the signals, spectra of the homo- and copolymers of 1,3,5-trioxane and 1,3,5-trioxepane with 1,3-dioxolane.[49]

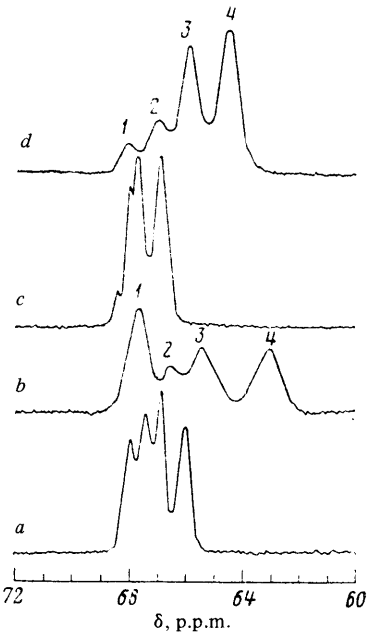


Figure 10. ^{13}C $\{^1H\}$ NMR spectra of the methine carbons of the VA units of a VC–VA copolymer (55 mole % VA) (*a*,*b*) and of the VP units of a VC–VP copolymer (70 mole % VP) (*c*,*d*) before (*a*,*c*) and after (*b*,*d*) the addition of $Pr(fod)_3$ in the ratio $Pr(fod)_3$:copolymer = 0.5. Solvent C_6D_6, temperature 50 °C. Assignment of the signals: *1*) VC–VA(VP)–VC, *2*) VC–VA(VP)–VA(VP), *3*) iso-VA(VP)–VA(VP)–VA(VP), and *4*) stable homotriads.[50]

In any case, the use of LSR in ^{13}C NMR spectroscopy improves the resolution of the signals, for example, $Pr(fod)_3$ has been used[50] to separate the methine signals of copolymers of vinyl chloride (VC) with vinyl acetate (VA) and vinyl propionate (VP). The ^{13}C NMR spectra (Fig.10) show that

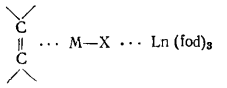
when $Pr(fod)_3$ is added, the methine signal separates into four peaks, corresponding to different triad configurations.

An approach analogous to that described for copolymers has been used to study the distribution of epoxide groups in epoxy-*cis*-polybutadiene and epoxy-*cis*- and epoxy-*trans*-polypentene polymers with different degrees of epoxidation by ^1H [51] and ^{13}C [52] NMR spectroscopy. When $Eu(fod)_3$ was added to the polymer solution, the signals from the $-CH_2-\underset{O}{C}-\underset{O}{C}$, $-CH_2-C=C-$, and $-CH=CH-$ groups separate into signals from the triad sequences of the epoxidised (E) and non-epoxidised (N) units. The magnitude of the induced paramagnetic shifts of the signals increases in the series: NNN $\ll$ NNE < ENE; NEN < NEE < EEE; $-CH=CH-$ < $-CH_2-C=C-$ < $-CH_2-\underset{O}{C}-\underset{O}{C}-$ $\leqslant$ $-\underset{O}{CH}-\underset{O}{CH}-$. The calculation showed that the distribution of the epoxide units in the epoxypolyalkenylenes obeys Bernoulli statistics.

4. The Distribution of *cis*- and *trans*-Units in Polymers Not Containing Polar Groups

The shift reagent method has been widely used to analyse the micro-structure of polymers and copolymers containing units with polar groups. This method, however, can give useful information on the micro-structure of polymer chains containing double bands, but without polar groups. One of the methods of "depositing" the lanthanide on the polymer is by the selective chemical modification of the polymer chain, for example by epoxidation. It should be noted, however, that selective chemical modification involves considerable difficulty.

A recent paper[53] proposed the use, for alkenes, of lanthanide shift reagents combined with Ag, Pd, and Rh salts, which are capable of forming π-complexes with alkenes and complexes with lanthanides of the type:



where M is a metal atom, and X a group capable of coordinating to a lanthanide.

It has been shown possible[54,55] to "deposit $Eu(fod)_3$ on π-complexes of the double bonds of a polymer chain with $AgNO_3$. This method, based on the established[56] difference in the stability constants of the π-complexes of silver with *cis*- and *trans*-alkenes, makes it possible to distinguish *cis*- (C) and *trans*- (T) isomers, and also the diads CC, CT(TC), and TT without deuteriation and spin–spin decoupling for any working frequencies of the ^1H NMR spectrometer.

Fig.11 gives the ^1H NMR spectra of polybutadiene solutions before and after the addition of the $AgNO_3$–$Eu(fod)_3$ system. After the addition of the shift reagent, the signals from the methylene and alkene protons of polybutadiene are split into two (*cis*- and *trans*-) and three (CC, CT(TC), TT) components. The magnitude of the induced paramagnetic shift increases linearly as far as a mass ratio $Eu(fod)_3$: polybutadiene = 3 : 1, after which the relationship reaches a plateau, since possible coordination sites on the polymer molecule are exhausted.

Thus the use of LSR to analyse the micro-structure of macromolecular compounds and to investigate the mechanism of the polymerisation of those polymers in whose NMR spectra the signals from monomer or stereo-sequences are not resolved, is extremely effective. The determination of the

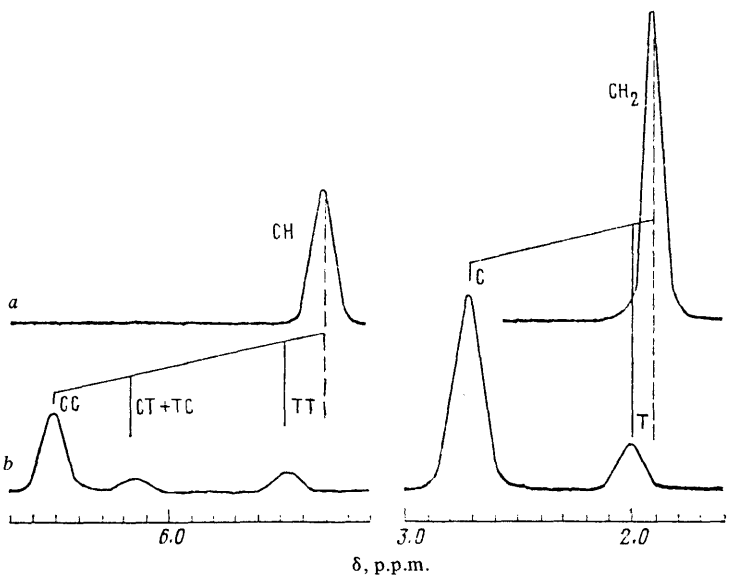


Figure 11. ^1H NMR spectra of a solution of polybutadiene in $CDCl_3$ before (*a*) and after (*b*) the addition of $AgNO_3$–$Eu(fod)_3$.[55]

correspondence of the chain growth to a particular statistic makes it possible to detect the influence of fine effects of intermolecular association[57] on the mechanism of polymerisation.

REFERENCES

1. F.Heatley, Nucl.Magn.Reson., 1980, **9**, 204.
2. J.C.Randall, "Polymer Sequence Determination ^{13}C NMR Method, Acad.Press, New York–San Francisco–London, 1977.
3. R.K.Harris, K.J.Packer, and B.J.Say, Macromol.Chem., 1981, Suppl 4, 117.
4. F.A.Bovey, "High Resolution NMR of Macromolecules" (Translated into Russian), Izd.Khimiya, Moscow, 1977, p.164.
5. D.Y.Yoon and P.J.Flory, Macromolecules, 1977, **10**, 562.
6. N.Bloembergen and W.C.Dickinson, Phys.Rev., 1950, **79**, 179.
7. H.M.McConnell and R.E.Robertson, J.Chem.Phys., 1958, **29**, 1361.
8. I.Solomon, Phys.Rev., 1955, **99**, 559.
9. B.Bleaney, J.Magn.Reson., 1972, **8**, 91.
10. C.C.Hinckley, J.Amer.Chem.Soc., 1969, **91**, 5160.
11. I.Ya.Slonim and A.Kh.Bulai, Uspekhi Khim., 1973, **42**, 1976, [Russ.Chem.Rev., 1973(11)].
12. J.Reuben, in "Progress in NMR Spectroscopy", Pergamon Press, New York, 1973, Vol.9, Part 1, p.1.
13. "NMR Shift Reagents" (Edited by R.E.Sievers), Acad.Press, New York, 1973.
14. K.G.Orrell, in "Annual Reports on NMR Spectroscopy", Acad.Press, London, Vol.9, p.1.
15. V.F.Zolin and L.G.Koreneva, "Redkozemel'nyi Zond v Khimii i Biologii" (Lanthanide Probes in Chemistry and Biology), Izd.Nauka, Moscow, 1980.
16. L.I.Barsukov, Yu.E.Shapiro, A.V.Viktorov, V.F.Bystrov, and L.D.Bergel'son, Bioorgan.Khim., 1976, **2**, 1404.
17. G.A.Webb, in "Annual Reports on NMR Spectroscopy", Acad.Press, London, 1975, Vol.6, p.1.
18. A.R.Katritzky and A.Smith, Tetrahedron Letters, 1971, **21**, 1765.
19. J.E.Guillet, I.R.Peat, and W.F.Reynolds, Tetrahedron Letters, 1971, **38**, 3493.
20. S.Amiya, I.Ando, and R.Chujo, Polym.J., 1973, **4**, 385; 1974, **6**, 194.
21. R.Chujo, K.Koyama, I.Ando, and Y.Inoue, Polym.J., 1972, **3**, 394.
22. A.Kh.Bulai, A.G.Gruznov, Ya.G.Urman, L.M.Romanov, and I.Ya.Slonim, Vysokomol.Soed., 1974, **16A**, 2203.
23. Ya.G.Urman, I.Ya.Slonim, S.G.Alekseeva, R.S.Barshtein, and V.S.Kalinina, Vysokomol.Soed., 1975, **17A**, 1530.
24. A.Kh.Bulai, V.S.Kalinina, B.M.Arshava, Ya.G.Urman, R.S.Barshtein, and I.Ya.Slonim, Vysokomol.Soed., 1976, **18A**, 2472.
25. T.J.Okada, Polym.Sci., Polym.Chem.Ed., 1979, **17**, 155.
26. S.J.Angyal, D.Greeves, and V.A.Pickles, Chem. Communs., 1974, 589.
27. M.Iida, S.Hayase, and T.Araki, Makromolecules, 1978, **11**, 490.
28. C.G.D'Hondt and R.W.Lenz, J.Polym.Sci., Polym. Chem.Ed., 1978, **16**, 261.
29. H.R.Kricheldorf and W.E.Hull, Makromol.Chem., 1980, **181**, 507.
30. Y.Inoue and T.Konno, Makromol.Chem., 1978, **179**, 1311.
31. E.D.Vorontsov, A.F.Rusak, V.V.Gusev, E.E.Filippova, N.N.Nikolaev, and V.P.Evdakov, Vysokomol.Soed., 1979, **21A**, 1415.
32. Yu.E.Shapiro, in collected papers "Sovremennye Dostizheniya YaMR-spektroskopii Vysokogo Razresheniya" (Present Achievements in High Resolution NMR Spectroscopy), Izd.FAN, Tashkent, 1979, p.3.
33. Yu.E.Shapiro, O.K.Shvetsov, N.M.Mironova, and B.S.Turov, Abstracts, VI Int.Symp. on Magnetic Resonance. Banff, Alberta (Canada), 1977, p.51.
34. N.P.Dozorova, Yu.E.Shapiro, and N.D.Zakharov, Izv.Vys.Ucheb.Zaved.SSSR Khim.i Khim.Tekhnol., 1977, **20**, 428.
35. O.K.Shvetsov, N.M.Mironova, Yu.E.Shapiro, N.P.Petukhov, V.Yu.Erofeev, A.A.Ershov, N.P.Dozorova, T.D.Shivaeva, and B.F.Ustavshchikov, Faserforsch.u.Textiltechn., 1977, **28**, 217.
36. Yu.E.Shapiro, N.P.Dozorova, B.S.Turov, and O.K.Shvetsov, Zhur.Anal.Khim., 1978, **33**, 393.
37. Yu.E.Shapiro, O.K.Shvetsov, N.P.Dozorova, and A.A.Ershov, Vysokomol.Soed., 1978, **20B**, 328.
38. T.Suzuki, K.Mitani, Y.Takegami, J.Furukawa, E.Kobayashi, and Y.Arai, Polymer J., 1974, 6, 496.
39. T.Okada, M.Izuhara, and T.Hashimoto, Polymer J., 1975, **7**, 1.
40. Yu.E.Shapiro, N.P.Dozorova, N.M.Mironova, and T.G.Balyberdina, Vysokomol.Soed., 1981, **23A**, 1374.
41. V.Yu.Erofeev, N.M.Mironova, Yu.Yu.Musabekov, Yu.E.Shapiro, and B.F.Ustavshchikov, Vysokomol. Soed., 1978, **20B**, 63.
42. Yu.Yu.Musabekov, V.Yu.Erofeev, Yu.E.Shapiro, A.F.Moskvin, N.M.Mironova, and B.F.Ustavshchikov, Vysokomol.Soed., 1979, **21A**, 1938.
43. Yu.E.Shapiro, Yu.Yu.Musabekov, V.Yu.Erofeev, and N.M.Mironova, "VII Mezhdunarodnyi Simpozium "Polimery-80"" (International Symposium "Polymers-80"), Varna, 1980, p.60.
44. A.Natansohn, S.Maxim, and D.Feldman, Bull.Inst. Politehn.Iasi, sect.2: Chim.Ing.Chim., 1980, **26**, 83.
45. T.Okada and T.Ikushige, Polymer J., 1977, **9**, 121.
46. M.Matlengevich and E.Turska, "VIII Mezhdunarodnyi Mikrosimpozium po Polikondensatsii. Tezisy Dokladov" (Summaries of Papers Presented at the Eighth International Micro-symposium on Polycondensation), Alma-Ata, 1981, p.65.
47. Yu.E.Shapiro, O.K.Shvetsov, and B.F.Ustavshchikov, Vysokomol.Soed., 1976, **18B**, 736.
48. Yu.E.Shapiro, O.K.Shvetsov, N.P.Dozorova, and A.A.Ershov, Kolloid.Zhur., 1976, **38**, 943.
49. D.Fleischer and R.C.Schulz, Makromol.Chem., 1972, **152**, 311; 1975, **176**, 677.
50. T.Okada, K.Hashimoto, and T.Ikushige, J.Polym.Sci., Polym.Chem.Ed., 1981, **19**, 1821.
51. B.S.Turov, N.A.Koshel', Yu.E.Shapiro, Yu.Yu.Musabekov, V.N.Bykova, and E.L.Antonov, Vysokomol.Soed., 1981, **23B**, 216.
52. O.Hayashi, K.Kimura, Y.Ooi, and H.Ueno, Kobunshi Ronbunshu, 1980, **37**, 327; Ref.Zhur.Khim., 1980, 19S6.
53. D.F.Evans, J.N.Tucker, and G.C.De Villaridi, Chem. Communs, 1975, 205.

54. N.P.Prikazchikova, Yu.E.Shapiro, B.S.Turov, and V.A.Efimov, "Tezisy Dokladov I Vsesoyuznoi Konferentsii "Kauchuki Emul'sionnoi Polimerizatsii Obshchego Naznacheniya"" (Summaries of Papers Presented at the First All Union Conference on General Purpose Emulsion Polymerisation Rubbers), Izd.TsNIITENeftekhim, Moscow, 1982, p.94.
55. Yu.E.Shapiro, N.P.Dozorova, B.S.Turov, and V.A.Efimov, Vysokomol.Soed., 1983, **25A**, 712.
56. M.A.Muhs and F.T.Weiss, J.Amer.Chem.Soc., 1962, **84**, 4697.
57. K.Plochocka, J.Makromol.Sci., Rev.Makromol.Chem., C, 1981, **20**, 67.

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