

Zvonimir Janović, Ante Jukić, Otto Vogl*

University of Zagreb, Faculty of Chemical Engineering and Technology

*University of Massachusetts, Department of Polymer Science and Engineering

Spacer groups in macromolecular structures

ISSN 0351-187

UDK 678.5/.8

Author's Review / Autorski pregled

Received / Primitljeno: 21. 12. 2009.

Accepted / Prihvaćeno: 19. 4. 2010.

Abstract

Spacer groups are often an essential part of polymer structures, particularly functional polymers. Many physical, chemical and biological properties depend strongly on their size. They provide flexibility and fabricability in highly rigid polymers. They also provide accessibility of functional groups, crystallization of side chains, separation of groups from the main chain for efficient chemical reactions and other characteristics. They can be found in natural polymers where flexible spacer groups provide essential links for the stability of polypeptide structures. In our research work we have studied the effects of flexible side chains for side chain crystallization and flexible side groups for reactivity on synthetic polymers, particularly, polyaldehydes, polyolefins, poly(ethylene oxides), poly(ω -alkenoic acid esters) and poly(alkyl methacrylates). Ultimately, we have shown some interest in how flexible links behave because of their oligomeric nature. The importance of short spacer groups on the crystallization of stereoregular polymers could possibly influence the stereospecificity of the addition to the catalyst site, for example, in propylene polymerization. In this paper we are trying to show, on a few demonstrative examples, the importance of spacer groups in macromolecular structures.

KEY WORDS:

functional polymers
 polyaldehydes
 poly(alkyl methacrylates)
 poly(ethylene oxides)
 polymer structure
 polyolefins
 poly(ω -alkenoic acid esters)
 spacer groups

KLJUČNE RIJEČI:

funkcijski polimeri
 polialdehidi
 poli(alkil-metakrilati)
 poli(esteri ω -alkanskih kiselina)
 polimerna struktura
 poli(oksi-etileni)
 poliolefini
 razmakne skupine

Razmakne skupine u strukturi makromolekula

Sažetak

Razmakne skupine bitna su odrednica strukture i svojstava funkcijskih polimera. Mnoga fizička, kemijska i biološka svojstva znatno ovise o njihovoj veličini. Određuju elastičnost i preradljivost vrlo krutih polimernih sustava, sklonost kristalizaciji temeljnih i bočnih skupina, kemijsku reaktivnost funkcijskih skupina, kao i mnoga druga svojstva. U biološkim makromolekulama elastičnost razmaknih skupina odgovorna je za stabilnost polipeptidnih struktura. Tijekom vlastitih istraživanja određen je utjecaj razmaknih skupina većeg broja sintetskih polimera, posebice polialdehida, poli(oksi-etilena), poliolefina, poli(estera ω -alkanskih kiselina) i poli(alkil-metakrilata) na sklonost kristalizaciji bočnih skupina i kemijsku reaktivnost. Prikazan je utjecaj kratkolančanih razmaknih skupina na stereospecifičnu orijentaciju monomernih molekula prema aktivnim koordinacijskim katalitičkim centrima i nastajanja kristalnih izotaktnih struktura na primjeru polimerizacije polipropilena.

Introduction

Polymers with functional groups are of great interest, because they impart specific chemical, spectroscopic and mechanical polymer properties. Many have been synthesized where the active groups are liquid crystals, catalysts for chemical reactions or hydrogenations. Polymeric UV absorbers, antioxidants, polymers with photo-, thermo- and electro-active as well as biologically active groups¹ have also been prepared. Such polymers may include homopolymers and copolymers, polymers of various additional characteristics: specific solubility, swellability or even completely insoluble materials; they also include oligomers or polymers of low, medium and high molecular, or specially designed molecular weights or molecular weight distributions. Functional polymers have been prepared in order to modify such basic chemical and physical properties as glass transition temperature, melting point, solubility, crystallinity and other fundamental properties, which depend directly upon steric requirements, polarity and interaction of functional groups. It has been estimated that polymers in the health and food industry and for the production and preservation of energy, will be the main thrust of the research development in polymer science over the next decade; as polymer engineering, polymer physics and polymer chemistry, respectively, were important in the development of polymer science in each of the preceding decades.

In this discussion examples of spacer groups influence on properties of some typical functional polymers based mostly on our own research activities are presented. Spacer groups provide accessibility of functional groups, crystallization of side chains, separation of groups from the main chain for efficient reactions and other characteristics. They can be found in natural polymers where flexible spacer groups provide essential links for the structure configuration and stability of polypeptide structures.

There has been tremendous attention paid to the influence of the kind and size of spacer groups. The reactivity of a functional group may be low when it is directly attached to the main chain, which may be a result of steric hindrance by the polymer backbone and neighboring side groups. Vogl and others^{2,3} described the effect of spacer groups in different

applications separating the functional groups from the backbone chain. Spacer groups may be either flexible or stiff. In general, they provide flexibility and allow the reactive group to react independently from the main chain. Thus, liquid-crystalline, mono-substituted acetylenes containing terphenyl pendent groups with methylene groups of varying spacer lengths and their polymers were synthesized.⁴ The polymer with long spacers (hexamethylene), formed a nematic mesophase when heated and cooled; however, the polymer with short spacers (methylene) could not exhibit liquid crystallinity at elevated temperatures. G. Luckhurst⁵ has employed the molecular field theory to predict the variation of the transitional properties of liquid crystal cyanobiphenyl dimers with the length of the spacer. He found that for spacers containing about 12 or more atoms, the odd-even effect predicted for the transitional properties varies significantly depending on the model used to describe the spacer conformation; that is, whether the torsional angles defining the conformations is taken to be discrete or continuous. In recent years, there have been intense efforts to develop methods to recover and reuse homogenous catalysts.⁶ Among these methods; the use of low molecular weight soluble linear polymers or dendrimers as supports have become attractive approaches since the supported catalysts are in the same phase as the reactants. In order to increase the accessibility of the catalytic sites, a spacer is often placed between the soluble polymer and the catalyst. The spacer units are mostly chosen to suit the chemistry of the end group on the polymer. It was shown that the reactivity and selectivity of this type of polymer-supported catalyst is dependent on the nature of the spacer.

Natural polymers

Nature has carefully selected spacer groups in their polymer structures and for our life. Nucleic acids are polyphosphoric acids, which are linked by pentoses to the bases of purines, and pyrimidines that ultimately form the double helix. Proteins are convincing examples of how flexible spacers, methylene spacer groups, dominate the conformation of the tertiary and quaternary structure of large protein molecules.⁷ Most consist of complicated structures, β -helices of poly(α -amino acids) connected with random α -amino acid chains (Fig. 1).

The α -amino acid units have spacer groups, methylene units, between the peptide chain and the functional group: i) a carboxylic group in glutamic acid, ii) an amino group in lysine and ornithine, and iii) a short hydrocarbon chain in leucine and isoleucine (whose *function* is to provide the hydrophobic interactions that stabilize secondary structure in proteins). The stunning discovery of Kauzman in the 1950s showed that hydrophobic portions for the macromolecule, such as leucine, isoleucine and phenylalanine interact and are capable of associating in hydrophobic clusters (Fig. 2).⁸ They are substantially responsible for the fragile poly(α -amino acid) structures in aqueous medium in the region of $37^\circ\text{C} \pm 10^\circ\text{C}$, in which we exist; above this temperature, denaturation of the proteins occurs.⁹

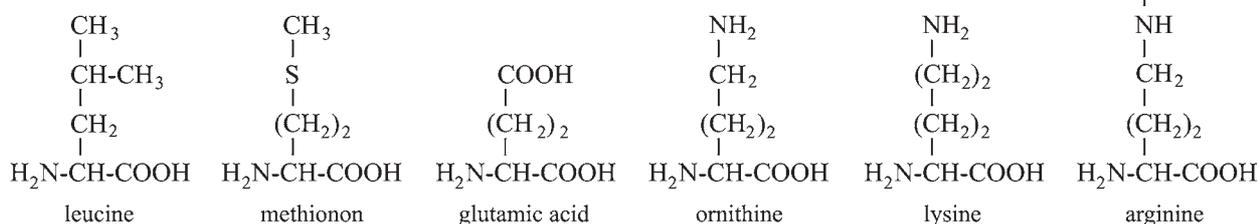


FIGURE 2 – The spacer groups in some selected α -amino acids⁸

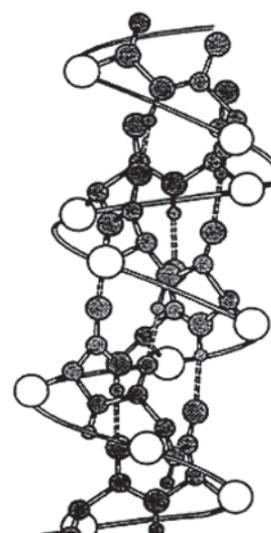


FIGURE 1 – Typical helical structure of protein molecule⁷

Some of the basic amino acid units have functional groups, such as amino, thio, and carboxylic acid groups. They are attached to the chiral α -carbon atom of the amino acid with 2 or 4 methylene units. Examples are lysine, ornithine, arginine, threonine and glutamic acid. Having the advantage of flexible links, they are now free to interact with other parts of the macromolecule, not necessarily with one in the vicinity. Of the 20 protein amino acids, 16 have a methylene group at the β - position, and a further three bear a methine group. No aromatic, carboxamido-, carboxylic carbon, or heteroatoms are attached directly to the α -carbon atom, but they are separated by this methylene or occasionally by a longer n-alkylene spacer group. The appearance of and the role played by the spacer group are discussed in an evolutionary context. P. Tompa¹⁰ by studying the role of a spacer group in the protein amino acid, has concluded that the general role of the spacer group is to ensure the uniformity of the constant regions $\text{H}_2\text{N}-\text{CH}-[(\text{CH}_2)_n-\text{R}']-\text{COOH}$ and the individuality of the R' contact groups by spatially separating them. Polysaccharides, carbohydrates, are used for nutritional purposes such as cellulose, starches and sugars. To prevent water from evaporating from fruits and vegetables, the skin of several fruits and vegetables are composed of esters of high aliphatic fatty acids of cellulose. Examples of such fruits are apples, pears, and cherries and of such vegetables tomatoes, peppers and cucumbers.

Side chain crystallization

Isotactic polyaldehydes

Isotactic polyaldehydes crystallize in helical conformations in different helices, depending on the size of spacing groups. Polyformaldehyde (polyoxymethylene) crystallizes in a 2_1 helical conformation with a

melting point of 178°C. Higher polyaldehydes with linear aliphatic side chains crystallize generally in 4₁ helices. Polyacetaldehyde melts at 165°C, poly(propionaldehyde) at 185°C and poly(n-butyaldehyde) at 225°C.^{11,12} The 4₁ helical crystalline structure for poly(n-heptaldehyde) is shown in Figure 3.¹³

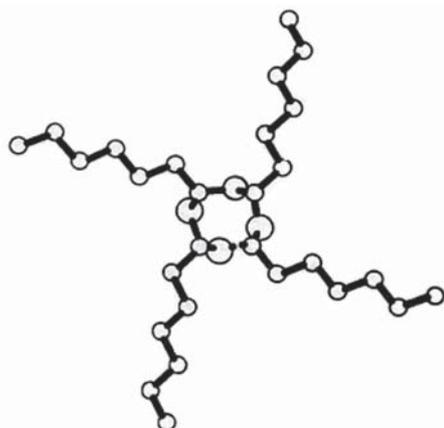


FIGURE 3 – Helical 4₁ structure of isotactic poly(n-heptaldehyde)¹³

From poly(n-valeraldehyde), a second transition point is observed, which we have identified as a transition of crystallization of the paraffinic side chain. It occurs in the region of 60-80°C. The higher melting transition in the region of initially 120-150°C is assigned to the melting of the polyacetal helix. The second transition is the transition (melting) of the paraffin side chain (Figure 4).¹⁴⁻¹⁶

The exact values of the transition (melting points of polyaldehydes and polyolefins) are shown in Figure 5. After poly(n-octaldehyde) the polyacetal melting around 120°C of the initially prepared polymer is no longer observed. But on annealing for a day above the transitions of the paraffinic melting transition or after solid-state extrusion, the polyacetal transition shows up clearly as a small but distinguishable transition peak. In addition, in thermal or mechanical treatment, the original peak of the paraffinic transition temperature splits into one major and one or two minor peaks, only a few degrees temperature separated, indicating a slightly different crystal alignment of the linear paraffinic side chains. After poly(n-nonanaldehyde) no more transition temperature peak that could be assigned to the polyacetaldehyde part of the crystalline isotactic polyaldehyde could be observed under any treatment.

It should be noted that the polymer of the branched isobutyraldehyde has a high melting point (dec.) of 305°C. This means that bulky side chains of the aldehyde monomer produced an isotactic polymer with a very rigid helix and consequently high melting point.

Higher aliphatic aldehydes polymerize well with anionic initiators, such as lithium tert-butoxide below their ceiling temperature (usually below

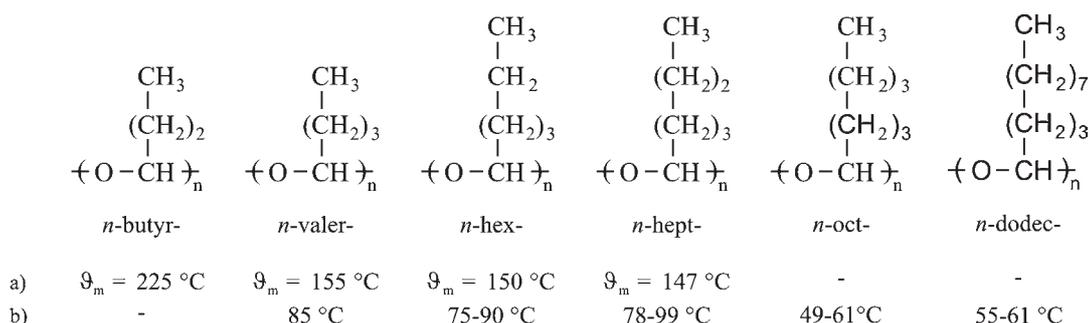


FIGURE 4 – Melting behavior of: (a) isotactic polyaldehydes (b) paraffin side chain¹⁴

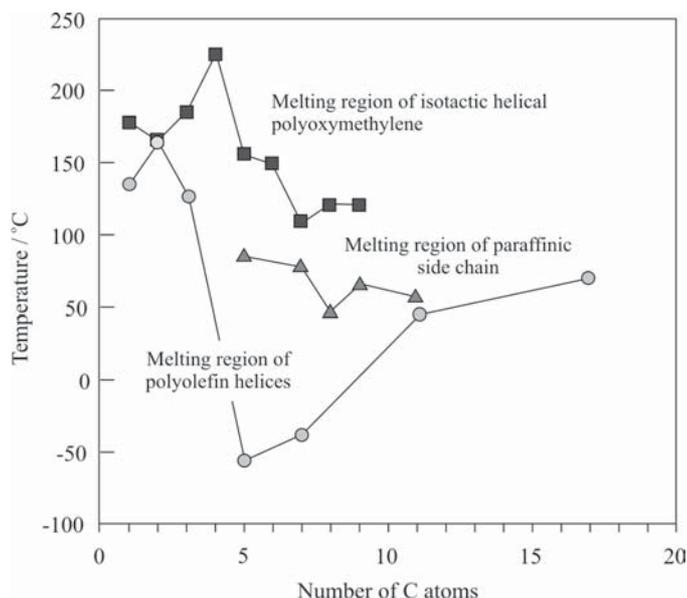


FIGURE 5 – Comparison of melting transitions of linear higher aliphatic isotactic polyaldehydes and polyolefins^{14,17}

-40°C) of polymerization and the polymers can be end capped to improve their thermal stability. The polymerization up to now has been limited to *n*-undecaldehyde because the melting point of the aldehyde is above the low temperature required for polymerization. Once the aldehyde's melting temperature is above the ceiling temperature of its polymerization it is difficult to induce polymerization effectively. Polymerization of higher aliphatic aldehydes with cationic initiators above the ceiling temperature results in cyclotrimerization to 2,4,6-tri-*n*-alkyl-1,3,5-trioxanes, crystalline with higher aldehydes. The trimer of *n*-nonaldehyde melts at 36°C, that of *n*-decaldehyde at 48°C, *n*-undecaldehyde at 56°C, and *n*-dodecaldehyde at 61°C. They all show one sharp transition point.

Isotactic polyolefins

It was intriguing to compare the transition (melting) points of isotactic polyaldehydes with those of polyolefins.¹⁷ Crystalline isotactic polyolefins have a 3₁ helical structure. Polypropylene melts at 165°C and poly(1-butene) at 126°C. It has several different crystalline forms, some melt as high as 134°C. Linear polyethylene melts at 136°C and is not helical but has an extended chain structure.¹⁸ The next few isotactic polyolefins melt at much lower temperatures, apparently because of interactive effects of the longer side chains of the isotactic polyolefins with the main chain of the polyolefin helix. As the length of the side chain of the isotactic polyolefins increases to poly(*n*-nonene) the melting transition reaches the level of the paraffinic side chain transition of the isotactic polyaldehydes. In other words, the melting transitions are determined by the melting transition of

the paraffinic side chains. As in the one case of the melting transition of polyaldehydes, isotactic polyolefins with bulky side groups, like poly(3-methyl pentene) or poly(3,3-dimethyl butene) have high melting points, in the range of 300°C.

Others

It should be mentioned that melting points of polymers in the range of 40-60°C have been recognized by Platé and his group in the early 70s.¹⁹ They studied poly(*n*-dodecyl methacrylate), an atactic polymer as far as the polymer main chain is concerned, and found it to be a crystalline polymer melting around 40°C. Clearly it was a classic example of polymer that was crystalline because it had a linear paraffinic side chain that was capable of crystallizing as a paraffinic side group. Janovic et al.²⁰ studied side-chain crystallinity in the scope of research of polymeric additives for lubricating mineral oils. It was found that increase of the content of crystalline phase i.e. long-chained alkyl methacrylates in copolymer (Figure 6), lowered the pour point of oil solutions, thus confirming that the side long-chained groups of *n*-alkyl methacrylate are an active component of the copolymer that reduces the mineral oil pour point. Therefore, the content of crystalline phase may be directly associated with pour point values of mineral oil solutions. The length of the alkyl group in *n*-alkyl methacrylates also influenced the monomer copolymerization reactivity and polymerization rate.²¹⁻²³

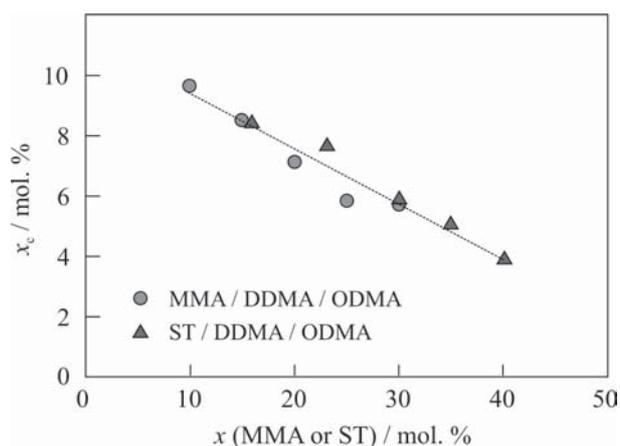


FIGURE 6 – Crystalline phase content in dependence on styrene / dodecyl methacrylate / octadecyl methacrylate (ST/DDMA/ODMA) or methyl methacrylate / dodecyl methacrylate / octadecyl methacrylate (MMA/DDMA/ODMA) terpolymer composition^{21,22}

The azobenzene monomers containing methacrylate groups varied by having alkyl spacers of varying lengths and, either nitro or methoxy substituents in conjugation with the azo groups, were polymerized via atom transfer radical polymerization (ATRP).²⁴ The kinetics of ATRP for each azo monomer was also studied. The effects of the types of substituents and the length of the spacer of the methacrylate monomers and the effect of molecular weight on the property of polymers were established.

Influence of spacer groups in functional polymer

Polymer structures

In our studies of the transitions of polyolefin carboxylates we have particularly concentrated on the paraffinic melting transition of poly(ω -hexenoates) and poly(ω -undecenoates). Poly(methyl ω -hexenoate) shows no transition in the 40 to 60°C range but poly(methyl ω -undecenoate) does. This again demonstrates, that, with a sufficiently long methylene grouping

from the polymer main chain, crystallization between the main chain and the functional end group, a kind of side chain crystallization can occur, if the spacer group is three methylene groups longer.

We have another significant observation relevant to the question: How long does the propylene oligomer chain have to be before crystallization can occur? We have carefully studied the embryonic state of the polymerization of trichloroacetaldehyde (chloral).²⁶ Chloral does not directly resemble propylene as the monomer but the initial state of its polymer formation could be readily investigated and we have studied it extensively. The purpose of this study was to understand and establish the influence of the size (diameter) of the side group (trichloromethyl) on the forced stereospecificity based on size alone. We found that chloral polymerizes to an exclusively stereospecific and conformational specific polymer, with a turn angle of the helix of 97.3° and an 11₃ helical structure. In the first addition of the chloral monomer unit to the (anionic) catalyst, the polymerization is not stereospecific. The first addition is, as expected, a 50:50 addition to the achiral initiator. As further addition of the monomers to the first addition products proceeds, the stereochemistry of addition is first favored and then forced (without any additional coordinative force) into a stereospecific and conformational specific crystalline polychloral. This occurs after the first turn of the helix, in other words after the pentamer or hexamer is formed, further addition of chloral is completely stereospecific and conformationally specific. We have now two arguments. In the case of the *paraffin* crystallization of polyaldehydes we require five methylene units before crystallization of the side chain can occur. This, of course is a random paraffinic crystallization, as is the case in the crystallization of the higher poly(ω -alkenoates). In the case of embryonic state of chloral polymerization we found that about five monomer units are needed to begin to form the helix. We would like to call this phase, the *amorphous* phase.

Polymerizations

Methyl ω -alkenoates were prepared from commercially available ω -alkenoic acids or the ω -alkenoic acids were synthesized (Figure 7).²⁵ The acids were esterified with methanol in high yields and epoxidized. The epoxidation of the higher ω -alkenoates proceeded in nearly quantitative yield (Figure 8). The relative ease of epoxidation of ω -hexenoate, which is essentially the same as olefin epoxidation has made higher ω -alkenoic acids and their epoxides attractive monomers (Figure 9).²⁷

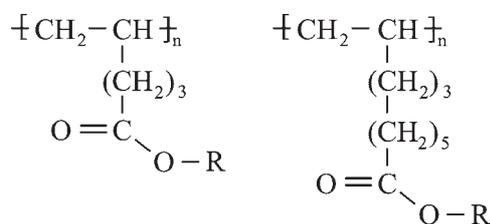


FIGURE 7 – Structure of poly(ω -alkenoic acid) carboxylates²⁵

One important surprise occurred when we recognized that the cause of the difference in the reactivity between methyl acrylate and higher methyl ω -alkenoates could be identified by the ¹³C NMR spectra of the methine carbon atom in the olefin group of the ω -alkenoates and the oxirane methine carbon of the ω -alkanoate as well as the carbonyl carbon atom of the carboxylate group (Figure 10).²⁸⁻³³

The ¹³C NMR spectra showed remarkable chemical shift (δ) changes of the methine C-atoms and carbonyl carbons as methylene groups were added between the olefinic double bond and the oxirane ring and the

carboxylate group. While the methine ^{13}C NMR chemical shift value of ethyl glycidate was $\delta = 48$, methyl 3-epoxybutanoate also $\delta = 48$, methyl 4-epoxypentanoate was $\delta = 53$ and methyl 5-epoxyhexanoate was also of $\delta = 52$.

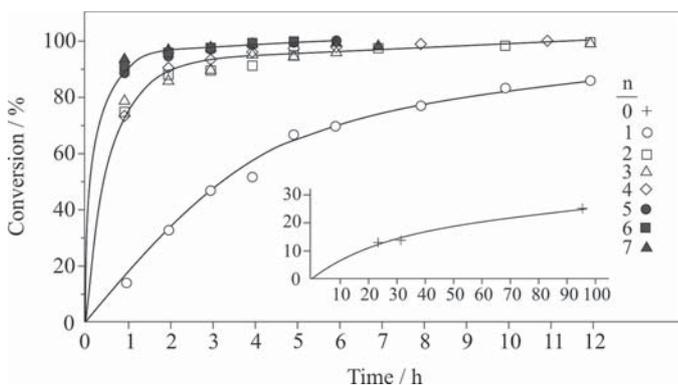


FIGURE 8 – The influence of the size of spacer group (n) on the rate of epoxidation of methyl ω -alkenoates³⁰

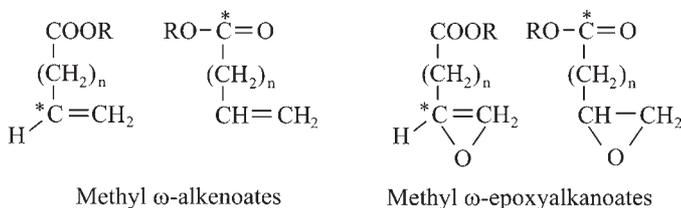


FIGURE 9 – Structures of methyl ω -alkenoates and methyl ω -epoxyalkanoates monomers³¹

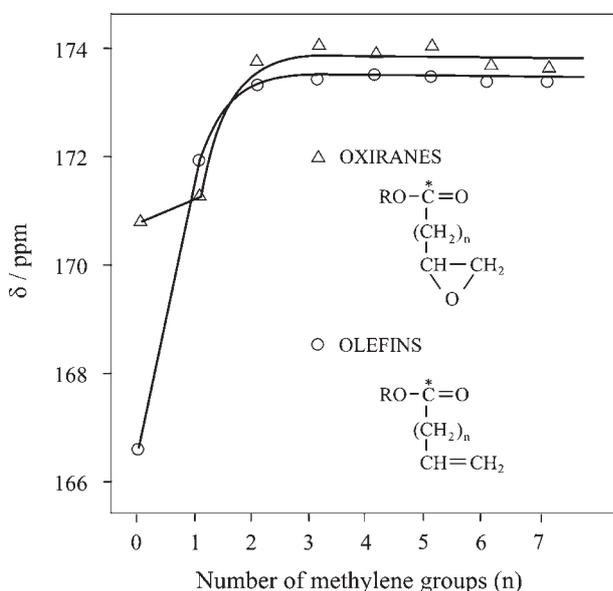


FIGURE 10 – ^{13}C NMR chemical shift values (δ) of carbonyl carbons of oxirane and olefin monomers depending on number of methylene groups³²

The chemical shift values of epoxy esters with longer methylene spacer groups level off at about $\delta = 52$, demonstrating the higher electron density on the methine carbon atom with increasing methylene groups shielding it from the carboxylate electron withdrawing effect (Figure 11). A similar effect was noticed with the chemical shift values of the ^{13}C NMR of the carbonyl carbon of the polymerizable groups when the

functional carbomethoxy groups were separated by about 3 methylene spacers (Figure 11).

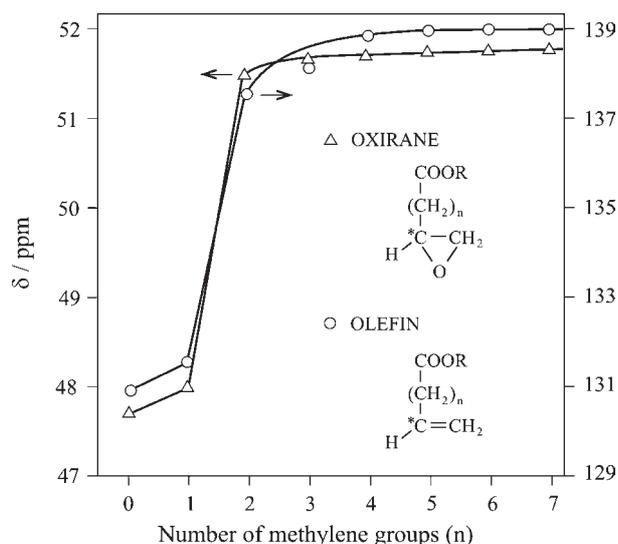


FIGURE 11 – ^{13}C NMR chemical shift values (δ) of methine carbons of oxirane and olefin functional monomers³³

What was anticipated from the NMR spectra was also found when the appropriate esters of the ω -alkenoic acids and ω -epoxyalkanoic acids were subjected to polymerization. The polymerization rates were slower at the monomers with the lower monomeric esters and leveled out, when the side chain reached three methylene spacer units. From that point the ω -alkenoate esters acted like regular α -olefins and the ω -epoxyalkanoates like regular epoxides.

Polymer reactions

Functional groups in polymers, when attached directly to the polymer chain have been known to react differently than functional groups in low molecular molecules. This different behavior had sometimes been called *polymer effect*. The question of the influence of the main polymer chain on the efficiency of substitution reaction certainly goes back to the study of hydrolysis of poly(methyl methacrylate).¹³ It became clear that the reactivity of these groups significantly depended on how close they were to the polymer main chain and what reactions were involved. Some time ago, we undertook a careful study^{14,16,26-29} on the influence of the chain length between the functional group and the backbone chain. We have chosen methylene spacers and compared the more flexible poly(oxy ethylene) with the polyethylene backbone chain. In the case of the poly(oxy ethylene) derivatives, it was found that the polymerizability of the ω -epoxycarboxylate increased as the function of the methylene spacer length (n) increases¹⁷ and reaches a plateau after n-3. With the polyolefin family, the polymerizability of α -olefin carboxylate²⁷ also increased, but it did not reach a plateau until one or two methylene spacer groups were added.

Polymers of poly(oxy ethylene) and polyethylene esters were hydrolyzed to the corresponding ionomers and converted to the free polymeric acids. Studies were also undertaken to investigate the polyanion – polycation complex formation as a function of backbone flexibility and side chain length.²⁹ It is known how difficult it was to hydrolyze poly(methyl methacrylate) quantitatively, how complicated it was to dehydrohalogenate PVC and how complicated it was to react poly(vinyl alcohol) with n-butyraldehyde quantitatively - and all that because of the dominating influence of the polymer chain. We have found that these problems can

be overcome, when polymers are used that have their reactive groups separated by flexible methylene spacer groups of at least 3 carbon atoms from the main chain.^{34,35} We have used carboxylic acid derivatives to demonstrate this effect. Reactions are nearly quantitative, like reactions on low molecular weight compounds. We found that the most effective derivatives of ω -alkenoic acids and ω -epoxyalkanoic acids were their imidazolids, which react quantitatively with amines and phenols. For a quantitative conversion of aliphatic alcohols to the ester it is better to use the lithium alkoxide.³⁴

Other polymer structures

Fluorocarbon chemistry was energized when it was found that the fluoroolefin group could be epoxidized. The most important compound that came out of this research was hexafluoropropylene oxide.³⁶ The significant breakthrough took place in 1959 with the discovery of hexafluoropropylene oxide. A whole new family of chemistry was developed around this discovery and led to important fluoroolefin polymers. Copolymers with tetrafluoroethylene, became very important. The important comonomers were fluoroolefins with a flexible spacer side group of a hexafluoropropylene oxide oligomer of about 2-3 oligomeric perfluorocarbon vinyl ethers groups terminated with sulfate ends on a tetrafluoroethylene backbone, usually at a ratio of 6:1.³⁷ It was the basis for the later development of polyfluorosulfonic acids with the trademark *Nafion* (Figure 12). This copolymer was discovered by Walther G. Grot in the late 1960s and was the first example of a fluorocarbon ionomer. Soon thereafter the corresponding carboxylate terminated fluoropolymers were commercialized.³⁸ These two types of fluorocarbon copolymers became the basis for the commercially important polyfluorocarbon sulfonates and carboxylates with the flexible fluorocarbon side chain.

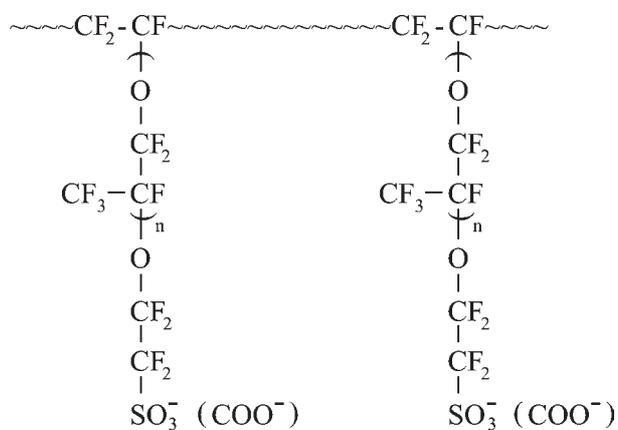


FIGURE 12 – Structure of ionomere on the base of sulfonated fluorocarbon (nafion)³⁷

H. Ringsdorf et al.³⁹ investigated multilayered Langmuir-Blodgett films of preformed polymers containing fluorocarbon side chains and hydrophilic spacer groups in the main chain. Results indicate that the side chain is tilted relative to the surface normal unlike their hydrocarbon analogues, which are perpendicular to the surface. The contribution of the rigid fluorocarbon side chain in this inherent thermal stability was discussed. The extent of orientation of the fluorocarbon side chain was specifically addressed as a function of backbone spacer length and sample temperature.

Importance of spacers in initial polymerizations

As it is well known, the isotactic polypropylene was discovered in the early 1950s by several groups using a transition metal catalyst consisting of TiCl_3 with aluminum alkyls as modifiers.⁴⁰ However, the primary credit goes to Natta and his research establishment.⁴¹ In 1957, *Montecatini* commercialized their invention. The polymerization was carried out in hexane as the solvent. This process produced about 10^4 g of polymer per milli-equivalent of the transition metal catalyst. Nearly 20 years later the so-called *high yield* catalyst systems based on the deposition of the transition metal catalyst onto magnesium chloride were discovered independently by *Montedison* in Italy and *Mitsui Petrochemicals* in Japan. This catalyst system produces 5×10^5 g polymer per milli-equivalent of transition metal.

The largest factors to determine the stereo-regularity and of the polypropylene molecule are the deposition of the transition metal compounds on MgCl_2 support and the use of electron donor compounds, which are considered to restrict the geometry of monomer coordination and polymer propagation (Figure 13a).⁴² In such a way, both the high stereoregularity and the high catalysts efficiency has been achieved. On the other hand, metallocene type catalysts have become commercially used recently. They stereoregularity is mostly determined by the ligand structure of the transition metal complex instead of the electron donor (Figure 13b).⁴²

Montedison improved the high yield catalyst system for the propylene polymerization in 1982 into the *Spheripol* process,⁴³ which is carried out in its initial stage in liquid propylene at 70°C and 40 bars and finished in the gas phase. Further, recent improvement is the *Borstar* process. Here, the first phase using TiCl_3 and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ as the catalyst, the *pre-polymerization* is carried out in a loop reactor under supercritical conditions of about 90°C and at pressures of about 50 bar followed by a second step in the gas phase. A different process, the gas phase process of propylene, is carried out directly in the gas phase at about $60\text{--}80^\circ\text{C}$.

The propylene polymerization proceeds by inserting the monomer propylene by a coordinative process into the transition metal alkyl bond. After a few monomer units are inserted into the growing transitional metal bonded oligomer chain it crystallizes (Fig. 14). The question now is: at

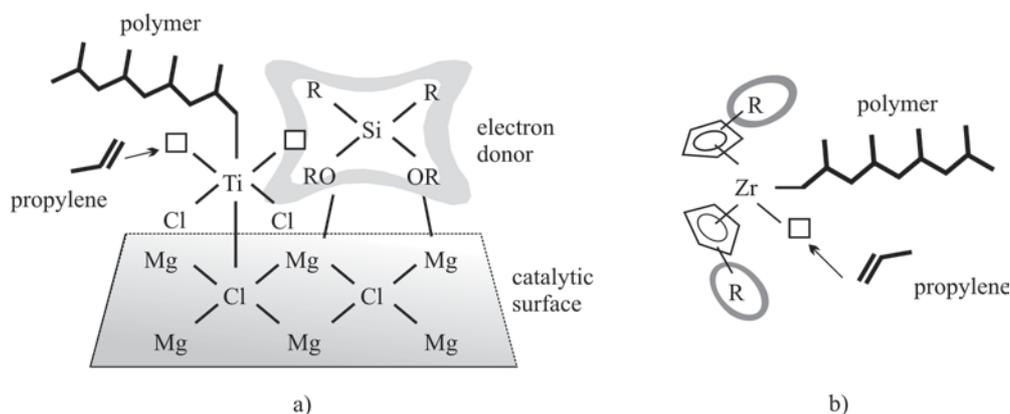


FIGURE 13 – Stereoregularity control models of propylene polymerization by (a) Ziegler-Natta supported MgCl_2 catalysts, (b) metallocene catalysts⁴²

what stage does crystallization occur and how many monomer units are needed for the stereospecific oligo-propylene chain to cause crystallization?^{18,44,45}

Polypropylene as a crystalline 3_1 helical structure was first determined by Corradini.⁴⁴ He found it to be a helix with three monomer units per repeat unit of 0.56 nm and a turn angle of the helix of 120°C. The polypropylene, when molded from the melt crystallizes and melts at 165°C. Further investigations on polyethylene found that the polypropylene helices restructure into folded chains with a fold length of about 14 nm (about 25 repeat units). The folded chain was first recognized in 1957.¹⁸ Polypropylene, like many crystalline helical polymers consists, for statistical reasons, of a 50:50 mixture of left and right-handed helices.



Transition metal catalyst

FIGURE 14 – Simplified scheme of the beginning of polypropylene crystallization during coordinative polymerization reaction of propylene¹⁸

In the late 60s several groups studied the x-ray structure of native (as-prepared) isotactic polypropylene.⁴⁶⁻⁴⁹ Let us assume that the polymerization occurs completely stereospecifically and all additions are either levo (or dextro) as expected from statistical considerations. At what time crystallization occurs and how many monomer units are needed to begin the formation of the crystalline structure of a 3_1 helix?⁵⁰ More importantly, does the polymer crystallization influence the stereochemistry of monomer addition at the monomer insertion stage?

Isotactic polypropylene, crystallized from the melt,⁵¹ is a semi-crystalline polymer with a crystallinity of about 60% and a melt temperature (or point) of about 165°C.⁵¹ The crystal modification has a repeat unit of 0.65 nm and consists of three phases (Figure 5): the α -phase (monoclinic) with a melt temperature of about 170°C, the β -phase (hexagonal) of about 155°C and the triclinic γ -phase⁵² for which several melt temperatures between 125°C and 150°C have been reported. The γ -phase crystallizes in the branching points of the spherulitic structure of the α -phase. The β -phase has to be nucleated and is not found in polypropylene, crystallized from the melt by spontaneous nucleation. The three phases differ from each other by slightly different arrangements of the left- and right-handed helices.

Conclusion

The importance of short spacer groups on the crystallization of stereoregular polymer could possibly influence the stereospecificity of the addition to the catalyst site. From the information that we presented above - side chain polymerization of aliphatic polyaldehydes, polymerization of ω -alkenoates and knowing that isotactic polypropylene crystallizes in a 3_1 helix, we propose that the polypropylene chain as it is grows from the active catalyst, requires 6-8 monomer units in the *amorphous* state to be able to begin crystallizing into the crystalline 3_1 helical structure. It is not clear whether or not the glass transition temperature of polypropylene, which is about -5°C, should be taken into consideration in this argument, because this temperature has only the meaning for phases not for oligomers with few monomer units and all processes are carried out above this temperature.

REFERENCES

- Vogl, O.: *Polymers with functional groups*, Pure Appl. Chem., 51(1979), 2409-2419.
- Vogl, O., Hatada, K., Kitayama, T. (Eds.): *Macromolecular design of polymeric materials*, Marcel Dekker Inc, New York, 1997.
- Kiliman, L. B., Deak, G., Vogl, O.: *Liquid crystalline polymers of polyolefin and poly (oxyethylene) derivatives*, J. Macromol. Sci. Pure Appl. Chem., A38(2001)4, 329-352.
- Zhou, D. et al.: *Synthesis and properties of polyacetylenes containing terphenyl pendent group with different spacers*, Macromolecules, 42(2009)5, 1454-1461.
- Luckhurst, G.: *Liquid crystals: a chemical physicist's view*, Liq. Cryst., 32(2005)11-12, 1335-1364.
- Anyanwu, U., Venkataraman, D.: *Effect of spacers on the activity of soluble polymer supported catalysts for the asymmetric addition of diethylzinc to aldehydes*, Tetrahedron Lett. 44(2003)6445-6448.
- Pauling, L., Corey, R. B.: *Configuration of polypeptide chain with favored orientations around single bonds*, Proc. Nat. Acad. Sci. USA, 37(1951)235.
- Kauzman, W.: *Some factors in the interpretation of protein denaturation*, Adv. Protein Chem. 14(1959)1-63.
- Bendu, D. A.: *Denaturation of protein*, Dictionary of Food and Nutrition, 2005.
- Tomba, P.: *On the appearance and role of space group in the protein amino acids*, J. Mol. Evol., 27(1988)147-153.
- Vogl, O.: *Polymerization of aliphatic aldehydes (1)*, J. Macromol. Sci., Chem. A, 1(1967)2, 243-266.
- Vogl, O.: *Polymerization of higher aldehydes*, Adv. Chem. Ser., 52(1966)67.
- Wood, J. S., Negulescu, I., Vogl, O.: *Higher aliphatic polyaldehydes. III. Crystal structure, crystallinity and melting transitions of isotactic poly(n-heptaldehyde)*, J. Macromol. Sci., Chem. A, 11(1977) (1), 171-194.
- Negulescu, I., Vogl, O.: *Higher aliphatic polyaldehydes. IV. Transitions in poly(n-valeraldehyde), poly (n-hexaldehyde), poly(n-heptaldehyde) and poly(n-octaldehyde)*, J. Polym. Sci., Polym. Chem. Ed., 14(1976)2995.
- Starr, J., Vogl, O.: *Higher aliphatic aldehyde polymers. VII. Poly(n-decaldehyde)*, Monatsh. Chem., 109(1978)1241.
- Starr, J., Vogl, O.: *Higher aliphatic aldehyde polymers. 8. Poly(n-undecanal)*, Makromol. Chem., 179(1978)2621.
- White J. I., Choi, D. D.: *Polyolefins - processing, structure development and properties*, Hanser, Munnich, 2005.
- Keller A.: *A note on single crystals in polymers: evidence of a chain folded configuration*, Phil. Mag., 2(1957)1161.
- Plate, N. A. et al.: *Interphase interaction in heterogeneous polymeric systems containing liquid-crystalline component*, Russ. Chem. Bull., 43(1994)1753-1769.
- Janovic, Z. et al.: *Lubricating oils pour point depressants based on alkyl methacrylate and styrene copolymers*, Fuels Lubr. (Goriva i maziva), 45(2006)3, 143-163.
- Vidović, E., Sarić, K., Janović, Z.: *Copolymerization of styrene with dodecyl methacrylate and octadecyl methacrylate*, Croat. Chem. Acta, 75(2002)3, 769-782.
- Jukić, A. et al.: *Terpolymerization kinetics of methyl methacrylate or styrene / dodecyl methacrylate / octadecyl methacrylate systems*, Polym. Int., 56(2007)1, 112-120.
- Šoljić, I., Jukić, A., Janović, Z.: *Terpolymerization kinetics of N, N-dimethylaminoethyl methacrylate / alkyl methacrylate / styrene systems*, Polym. Eng. Sci., 50(2010)3, 577-584.
- Li, N. et al.: *Synthesis and third-order NLO properties of polymethacrylates containing pendent azobenzene groups*, High. Perform. Polym., 19(2007)3, 356-367.
- Muggee, J., Vogl, O.: *Poly(alkylene oxide) ionomers VIII. Synthesis of methyl ω -alkenoates and methyl ω -epoxyalkanoates*, J. Polymer Sci., Polym. Chem. Ed., 22(1984)(10), 2501-2521.
- Vogl, O.: *Haloaldehyde polymers and macromolecular asymmetry*, J. Polymer Sci., Polym. Chem. Ed., 38(2000)(15), 2623-2634.
- Vogl, O., Muggee, J., Bansleben, D.: *Poly(alkylene oxide) ionomers V. Polymers and copolymers of cyclic ethers with pendant carboxylate groups*, Polym. J., 12(1980)9, 677-686.
- Vogl, O. et al.: *Polymers and copolymers of methyl ω -epoxyalkanoates. Part V of Poly(alkylene oxide) ionomers*, in *Coordination Polymerization* (Eds. Price, C.C., Vandenberg, E.J.), Polym. Sci. Tech., 19(1983), 95-109.
- Muggee, J., Vogl, O.: *Poly(alkylene oxide) ionomers IX. Polymerization of methyl ω -epoxyalkanoates and characterization of the polymers*, J. Polym. Sci., Part A: Polym. Chem., 24(1986)9, 2327-2349.
- Vogl, O. et al.: *Reactive groups, spacer groups and functional groups in macromolecular design*, J. Macromol. Sci., Chem. A, 21(1984)8-9, 1217-1235.
- Bansleben, D. A., Janović, Z., Vogl, O.: *Poly(alkylene oxide) ionomers: XIII. Copolymers of trioxane with the epoxide and 1,3-dioxolane of methyl 10-undecenoate*, J. Polym. Sci., Polym. Chem. Ed., 22(1984)11, 3263-3288.
- Purgett, M. D., Vogl, O.: *Functional polymers XLVIII. Polymerization of ω -alkenoate derivatives*, J. Polymer Sci., Polym. Chem. Ed., 26(1988)3, 677-700.

33. Vogl, O.; Kiliman, L. B.: *Poly(10,11-epoxyundecanoic acid), poly(5,6-epoxyhexanoic acid) and some of their derivatives*, J. Macromol. Sci. Pure Appl. Chem. A, 38(2001)2, 123-135.
34. Deak, G., Vogl, O., Kiliman, L. B.: *Poly(10-undecenoic acid) and some of its derivatives*, J. Macromol. Sci. Pure Appl. Chem. A, 38(2001)3, 221-231.
35. Kiliman, L. B., Deak, G.; Vogl, O.: *Liquid crystalline polymers of polyolefin and poly(oxyethylene) derivatives*, J. Macromol. Sci. Pure Appl. Chem. A, 38(2001)4, 329-352.
36. Resnick, P.: *Perfluoroepoxides* in Kirk Othmar *Encyclopedia of Chemical Technology*, Vol. 10, Third Edition, John Wiley, New York, 1980.
37. Mauritz, K. A., Moore, R. B.: *State of understanding of nafion*, Chemical Reviews 104(2004)4535.
38. Ukihashi, H., Yamabe, M., Miyake, H.: *Polymeric fluorocarbon acids and their applications*, Progr. Polym. Sci., 12(1986)229.
39. Ringsdorf, J. et al.: *Structural studies of polymers with hydrophilic spacer groups. 2. Infrared spectroscopy of Langmuir-Blodgett multilayers of polymers with fluorocarbon side chains at ambient and elevated temperatures*, Macromolecules, 22(1989)8, 3475-3480.
40. Moore, E. P.: *Polypropylene Handbook*, Hanser Verlag, New York, 1996.
41. Pino, P.: *The impact of the discovery of the polymerization of the α -olefins on the development of the stereospecific polymerization of vinyl monomers in Giulio Natta: Present Significance of His Scientific Contribution* (Eds: Carra, S., Parisi, F., Pasquon, I., Pino, P.), Edrice di Chimica Srl., 1982.
42. Muelhaupt, R.: *Catalytic polymerization and post polymerization catalysis fifty years after the discovery of Ziegler's catalysts*, Macromol. Chem. Phys., 204(2003)289-327.
43. Galli, P.: *Methods of controlling morphology for tailoring polymer properties, the Spheripole process*, J. Macromol. Sci. B, 35(1996)3, 427.
44. Natta, G., Corradini, P.: *Structure and properties of isotactic polypropylene*, Nuovo Cim. Suppl., 15(1960)40.
45. Bruckner, S., Meille, S. V.: *Non-parallel chains in crystalline - isotactic polypropylene*, Nature, 340(1969)455.
46. Blais, P., Manley, R.: *Morphology of nascent Ziegler-Natta polymers*, Science, 153(1966)539.
47. Wristers, J.: *Nascent polypropylene morphology*, J. Polym. Sci., Polym. Phys. Ed., 11(1973)8, 1601.
48. Guttman, J. Y., Guillet, J. E.: *Mechanism of propylene polymerization on single crystals of α -titanium trichloride*, Macromolecules, 3(1970)4, 470.
49. Vogl, O., Jaycox, G.: *Crystalline helical polymers*, Polimeri, 18(1997)3-4, 141-149.
50. Vogl, O.: *Polypropylene: an Introduction*, J. Macromol. Sci. Pure Appl. Chem. A, 36(1999)11, 1547-1559.
51. Lotz, B., Wittman, J. C., Lovinger, A.: *Structure and morphology of polypropylenes: a molecular analysis*, Polymer, 37(1996)4979.
52. Bruckner, S., Meille, S. V.: *non-parallel chains in crystalline γ -isotactic polypropylene*, Nature, 340(1989)6233, 455-457.

CONTACT

Dr. Otto Vogl
Herman F. Mark Professor Emeritus
Department of Polymer Science and Engineering
University of Massachusetts
Amherst, MA 01003-4350 U.S.A
E-mail: vogl@polysci.umass.edu

Poziv na sudjelovanje na XXII. hrvatskom skupu kemičara i kemijskih inženjera

Hrvatsko društvo kemijskih inženjera i tehnologa (HDKI) i Hrvatsko kemijsko društvo (HKD) organiziraju XXII. hrvatski skup kemičara i kemijskih inženjera, koji će se održati od 13. do 16. veljače 2011. u Zagrebu, u hotelu *Four Points by Sheraton Panorama*, pod pokroviteljstvom Sveučilišta u Zagrebu, Akademije tehničkih znanosti Hrvatske, Hrvatskoga inženjerskog saveza i Ministarstva zaštite okoliša i prostornog uređenja.

Namjera ovoga skupa je predstavljanje znanstvene i stručne djelatnosti iz područja kemije, kemijskog inženjerstva i srodnih znanstvenih disciplina, s naglaskom na promicanju interdisciplinarnosti te primjeni znanosti u razvoju naprednih materijala, zaštiti okoliša i razvoju održivih tehnologija. Na skupu će se okupiti brojni znanstvenici i stručnjaci sa sveučilišta, istraživačkih instituta, iz škola i industrije iz Hrvatske i inozemstva. Predstavljanje najnovijih dostignuća i razmjena iskustava putem plenarnih i pozvanih predavanja, predavanja nagrađenih znanstvenika te usmenih i posterskih izlaganja najdjelotvorniji su načini širenja novih znanja, ideja i tehnologija radi doprinosa razvoju gospodarstva. Sva priopćenja održana na skupu bit će tiskana u *Knjizi sažetaka*. Kao pridružena manifestacija, uz skup će se održati izložba kemijskoga industrijskog i laboratorijskog

pribora i instrumentacije, računalne opreme i programske podrške te literature.

Skup će raditi u sljedećim sekcijama:

1. Kemija
2. Kemijsko i biokemijsko inženjerstvo
3. Materijali
4. Obrazovanje
5. Zaštita okoliša
6. Dizajn kemijskih proizvoda.

Detaljnije informacije o skupu mogu se naći na internetskoj stranici 22skiki.fkit.hr.

Pozivamo vas da nam se pridružite na XXII. hrvatskom skupu kemičara i kemijskih inženjera te da svojim sudjelovanjem pridonese te njegovu uspjehu i kvaliteti.

Predsjednica Znanstveno-organizacijskog odbora
Vesna TOMAŠIĆ