Structure and Properties of Copolymers of Vinylcyclohexane and α-Methylvinylcyclohexane with Acrylonitrile

G. B. KHARAS, V. I. KLEINER, L. L. STOTSKAYA, G. P. KARPACHEVA, B. A. KRENTSEL, M. A. DZYUBINA, N. A. NECHITAILO, S. D. ARTAMONOVA, I. A. LITVINOV, V. F. CHIRKOVA, and L. D. VOLKOVA, *Institute of Petrochemical Synthesis. Academy of Sciences of the USSR, Moscow, V-71, U.S.S.R.*

Synopsis

A study has been made of the structure and properties of alternating equimolar and random copolymers of vinylcyclohexane and α-methylvinylcyclohexane with acrylonitrile using infrared and ^{1}H-NMR spectroscopy methods, as well as x-ray diffraction and differential thermal analyses. The spectral methods allowed an estimation of the composition and distribution of comonomer units in the copolymer macrochains. The thermal stability of alternating copolymers was found to be higher than that of polyacrylonitrile. Alternating and random copolymers are amorphous products with various dimensions of crystallites. Information on the molecular motion intensity and temperatures of structural transitions in copolymer macrochains was obtained by the spin-probe technique.

INTRODUCTION

The use of Lewis acids as complex-forming agents is known to allow the realization of copolymerization of α-olefins with polar monomers.[1-9] The copolymerization of vinylcyclohexane (VCH) and α-methylvinylcyclohexane (MVCH) with acrylonitrile (AN) in the presence[10] of $AlEtCl_2$ is one such example. We have shown that on the copolymerization of VCH and AN, copolymers are formed with alternating and random distribution of comonomer units, depending on the ratio between the concentration of the polar monomer and a complex-forming agent.

This paper is devoted to a study of the structure and properties of copolymers of VCH and MVCH with AN.

EXPERIMENTAL

Synthesis of copolymers of VCH and MVCH with AN was described in Ref. 10. The composition of copolymers was found according to elementary analysis data.

Infrared spectra were registered in the range 700–3200 cm^{-1} using a UR-10 spectrophotometer. Copolymer samples were thin films prepared by hot molding at 150°C. To calibrate spectra in the range 2000–2300 cm^{-1}, use was made of the spectrum of carbon oxide (with an experimental error within ~0.5 cm^{-1}); in other ranges, the spectrum of polystyrene was used.

^{1}H-NMR spectra of 10% solutions of copolymers in dimethylformamide-d_6

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were measured using a Varian T-60 spectrometer at 35°C with tetramethylsilane as an internal standard.

Differential thermal analysis (DTA) and gravimetric analysis (TGA) were carried out by use of a derivatograph of the Paulik-Paulik system. The temperature gradient was 3°C/min, the sample weight 150 mg.

The thermomechanic curves were obtained by using a Kargin dynamometric balance. The rate of temperature rise was 1°C/min.

The x-ray diffraction analysis of copolymers was conducted using an URS-60 type apparatus with Cu $K\alpha$ radiation. For this purpose, polymer samples were pressed to form films with thickness of ~0.5 mm. The x-ray patterns were obtained with flat plate cameras and photometered using a Carl Zeiss G-11 microphotometer.

The EPR spectra were recorded on an RE 1301 spectrometer at $\nu = 9300$ MHz. The accuracy of thermostatic regulation was ±1°C.

RESULTS AND DISCUSSION

Alternating and random copolymers formed as a result of copolymerization of VCH and MVCH with AN are white, amorphous powders which are well soluble in such polar solvents as dimethylsulfoxide, acetonitrile, and acetone and insoluble in n-heptane, cyclohexane, benzene, and toluene. Alternating equimolar copolymers of VCH and MVCH with AN also dissolve in chlorinated hydrocarbons (CH_2Cl_2, $CHCl_3$, CCl_3), whereas random copolymers containing more than 70 mol % of AN units have a limited solubility in these solvents.

Comonomer Unit Distribution in Copolymers

Copolymerization of VCH and MVCH with AN at AN/AlEtCl$_2$ = 1 results, as previously described,[10] in the formation of alternating copolymers of equimolar composition.

To study the structure of alternating copolymers of VCH and MVCH with AN, their infrared spectra were analyzed and compared with the spectra of polyacrylonitrile (PAN)[11] and isotactic and atactic polyvinylcyclohexane (PVCH).[12,13] On comparison of the infrared spectra of PAN and equimolar alternating copolymers (Fig. 1), one can see that a narrower band of stretching vibrations of the C≡N groups is observed for alternating copolymers which is located at 2234 cm^{-1} for VCH-AN copolymers and at 2233 cm^{-1} for MVCH-AN copolymers. (This band is rather wide in the spectrum of PAN, being at 2242.5 cm^{-1}.) A similar phenomenon, the shift of the stretching vibration band for C≡N groups to the longwave range, was also observed in the case of alternating copolymers of AN with styrene.[14] This makes it possible to conclude that in the copolymers synthesized, most AN units are distributed in an isolated manner. The absence of bands at 1600 cm^{-1}, which characterize vibrations of cyclized AN units[11] in the case of PAN, also seems to be related to the isolated distribution of AN units in the copolymers. As was shown earlier, the region 880–900 cm^{-1} in the spectra of PVCH and copolymers of VCH is very sensitive to the distribution of VCH units.[13] In spectra of isotactic and atactic PVCH, as well as in spectra of VCH-styrene[13] and VCH-methylpentene-1[15] copolymers with a high content of VCH units, a doublet is present at 892–885 cm^{-1} in this region.
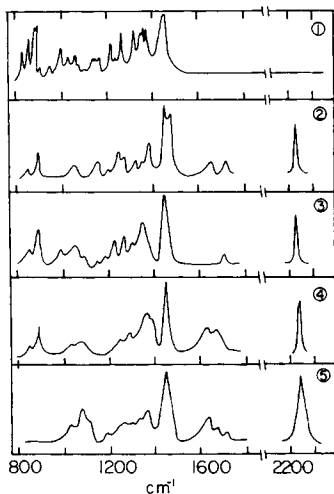
Fig. 1. Infared spectra of PVCH, PAN, VCH-AN, and MVCH-AN copolymers: (1) PVCH; (2) and (3) alternating, equimolar MVCH-AN and VCH-AN copolymers, respectively; (4) random VCH-AN copolymer with 75 mol % AN units; (5) PAN.

However, as the VCH content in the copolymer decreases, the intensity of the band at 885 cm^{-1} drops sharply, and only one band at 892 cm^{-1} remains in this region in the spectra of copolymers with a low content of units. A single band at 892 cm^{-1} is also present in this region in the spectra of equimolar, alternating VCH-AN copolymers, which can be considered as an evidence in favor of isolated VCH units in the chain. This conclusion agrees with the reactivity ratio values for VCH, being 0 at AN/AlEtCl$_2$ = 1.5–10.

The composition of VCH-AN copolymers prepared by copolymerization at AN/AlEtCl$_2$ > 1 depends on the composition of the initial comonomer mixture,[10] the VCH unit content being no more than 50 mol % in copolymers of various compositions.

A ratio between the intensities of the stretching vibration bands of the groups in the region 2230–2240 cm^{-1} and of the vibration band of the cyclohexyl ring at 892 cm^{-1} (D_{892}) obviously depends on the copolymer composition. This relationship can be used for spectroscopic determination of random VCH-AN copolymers. Taking into account that the halfwidth of the stretching vibration band of C≡N groups depends on the copolymer composition, one can use the integral intensity of the stretching vibration band of the C≡N groups ($A_{C≡N}$) as a criterion of the AN content in the polymer.

The composition and structure of copolymers of VCH and MVCH with AN can also be estimated from ^{1}H-NMR spectra. In the spectra of alternating VCH-AN copolymers with equimolar composition (Fig. 2), an unresolved peak in the range of 0.8–2.4 ppm is observed, as well as a broad peak in the range of 2.4–3.2 ppm. A comparison of the spectrum of the alternating VCH-AN copolymer with the spectra of PVCH[12] and PAN[16] allows one to assign the signal in the range of 0.8–2.4 ppm to absorption by protons of the VCH units in the copolymer. A shoulder in the region of 1.8–2.4 ppm can probably be assigned, by analogy with PAN (Fig. 2), to absorption by methylene protons of the AN units. The peak in the range of 2.4–3.2 ppm with a maximum at 2.8 ppm is due to absorption by methine protons of the AN units. The assignment of the peak
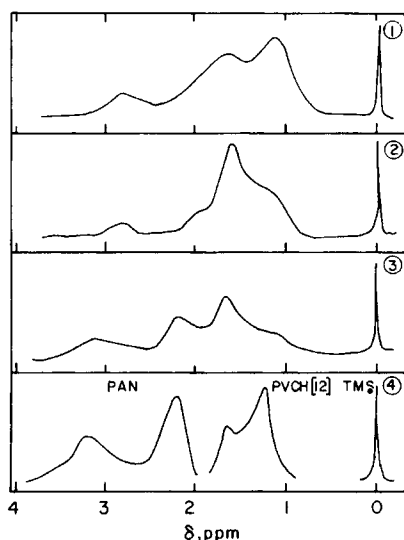
Fig. 2. ^{1}H-NMR spectra of PVCH, PAN, VCH-AN, and MVCH-AN copolymers; (1) and (2) alternating, equimolar MVCH-AN and VCH-AN copolymers, respectively; (3) random VCH-AN copolymer with 75 mol % of AN units; (4) PAN and PVCH.

in this region was made on the basis of the chemical shift value for methine protons of the AN units in ^{1}H-NMR spectra of PAN and copolymers of AN with vinylacetate, methacrylonitrile,[17] methylmethacrylate,[18] vinylchloride,[19] and styrene.[17,20] In the ^{1}H-NMR spectra of the VCH-AN copolymers prepared by copolymerization of comonomer mixtures of various composition at AN/AlEtCl$_2$ = 1, the ratio of the total area of proton peaks in the polymer chain and cyclohexyl ring (0.8–2.4 ppm) to the area of the methine proton (2.4–3.2 ppm) is a constant 16:1, which corresponds to the structure of the alternating copolymer with the equimolar composition:
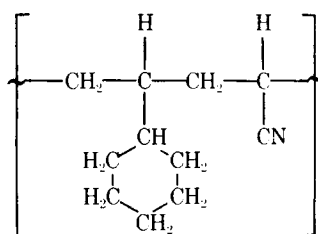

The assignment of the proton peaks in the ^{1}H-NMR spectrum of the alternating MVCH-AN copolymer was similar to the way for the case of the alternating VCH-AN copolymer. The ratio of the total area of the proton peaks of the macrochain, the methyl group, and cyclohexyl ring (0.8–2.4 ppm) to the area of the methine proton peak (2.4–3.2 ppm) in the spectra of MVCH-AN copolymers (prepared by copolymerization of comonomer mixtures of various composition at AN/AlEtCl$_2$ = 1) is constant 18:1 and corresponds to the structure

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TABLE I

Structure Parameters of Homopolymers and Copolymers of VCH and MVCH with AN

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Sample	2θ			Dimensions of crystallites, Å[a]
Atactic PVCH	7°59′;	11°07′;	17°50′	30
PAN			17°00	25
Alternating equimolar MVCH-AN		14°55′		33
Alternating equimolar VCH-AN	7°59′		17°00′	20
Random VCH-AN with 75 mol % AN			16°50′	27

[a] The crystallite dimensions were calculated from the Sherrer formula applied to the polymer systems: $L = 0.9\lambda/\beta \cos \Theta$.

of alternating copolymer having the equimolar composition:
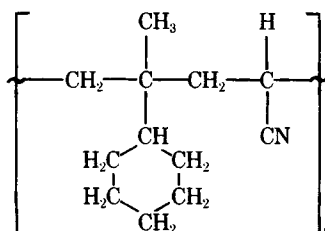
Comparison of the ^{1}H-NMR spectrum of the random VCH-AN copolymer containing 75 mol % of AN units with the spectra of the alternating copolymer (Fig. 2) shows that the area of proton peaks of VCH units in the spectrum of the random copolymer decreases, and a peak with a maximum at 2.2 ppm is observed, which is similar to the peak of methylene protons of AN units in PAN. The area of the peak of the methine proton in AN units also increases as compared to alternating copolymers. This fact, as well as the fact that the position of peaks of methine and methylene protons in AN units corresponds to the position of these peaks in PAN, indicates the presence of sequences of AN units in random VCH-AN copolymers.

Thus the data of infrared and ^{1}H-NMR spectroscopy are indicative of alternation of comonomer units in equimolar copolymers of VCH and MVCH with AN and confirm the presence of sequences of AN units and isolated VCH units in copolymers obtained at AN/AlEtCl$_2$ > 1.

X-Ray Diffraction Analysis of Copolymers

To study the structure of alternating and random copolymers of VCH and MVCH with AN, measurements of x-ray diffraction were conducted at large scattering angles. The maxima of amorphous halos and the dimensions of coherent scattering regions (dimensions of crystallites) of the homopolymers and copolymers of VCH and MVCH with AN are given in Table I. A comparison of crystallite dimensions in the alternating and random VCH-AN copolymers allows us to conclude that the presence of long sequences of AN units in the random copolymer with 75 mol % of AN units results in an increase of intermolecular order. The absence of a maximum in the region of angles 2θ = 7°–10° in the case of the random VCH-AN copolymer seems to be caused by separation of the VCH units by sequences of AN units.

Molecular Mobility

To obtain information on the molecular motion intensity and structural transitions which occur in macromolecules with variations of temperature, co-polymers of VCH and MVCH with AN were studied by the spin-probe technique. A stable iminoxyl radical having the structure (I) was used as spin probe. This radical (10^{-1} mol/l.) was

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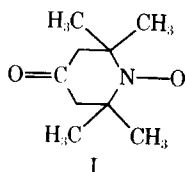
incorporated into the polymer by diffusion from vapor. The correlation time of the rotary motion of the spin probe (τ_c) was determined on the basis of pa-rameters of the EPR spectra of copolymers in a manner similar to the technique described in Ref. 21. Figure 3 presents the dependence of (τ_c) on temperature obtained from analysis of the EPR spectra of the spin-probe introduced into VCH-AN and MVCH-AN copolymers, whose rotational mobility depends on temperature and structure specific features of the polymer matrix.[22]

An increase of the correlation time of the spin-probe in the random copolymer seems to be related to the presence of AN unit sequences in the polymer chain, which causes greater intra- and intermolecular interaction. The domains cor-responding to the various laws of the correlation time τ_c variations can be easily seen on the curve of the temperature dependence (Fig. 3). The transient region may probably be attributed to the glass transition of the polymer (T_g).[21] The values of the glass-transition temperatures for MVCH-AN and VCH-AN co-polymers determined from the middle point of the mean part of the temperature dependence of τ_c (Table II) agree well with transition temperature values ob-tained from thermomechanical curves.

Thus the higher glass-transition temperature of the alternating VCH-AN copolymer as compared to that of the random copolymer can be explained by the greater rigidity of polymer chains.
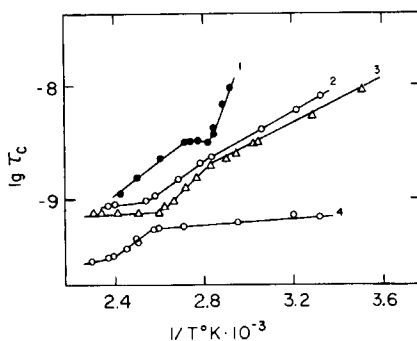
Fig. 3. Temperature dependence of the correlation time (τ_c) of the spin probe in polymers: (1) random VCH-AN copolymer with 75 mol % AN units; (2) and (3) alternating, equimolar MVCH-AN and VCH-AN copolymers, respectively; (4) atactic PVCH.

Sample	T_g, °C	
	Spin-probe	Thermomechanics
Atactic PVCH	118	—
Alternating equimolar MVCH-AN	107	106
Alternating equimolar VCH-AN	96	97
Random VCH-AN with 75 mol % AN	89	82

Thermal Properties of Copolymers

The thermal properties of VCH-AN and MVCH-AN copolymers, as well as PAN and atactic PVCH, were studied by the DTA method. From data presented in Table III, one can see that heating the homopolymers and copolymers of VCH and MVCH with AN in air results in thermo-oxidative degradation. Oxidation of equimolar, alternating VCH-AN and MVCH-AN copolymers begins at 295 and 275°C, respectively, which exceeds the temperature of the onset of oxidation of both PAN and atactic PVCH by more than 100°C. Lesser thermo-oxidative stability of MVCH-AN alternating copolymer as compared to VCH-AN copolymers seems to be due to presence of CH_3 groups in the MVCH units. The alternating VCH-AN equimolar copolymer is the most stable, its thermal stability being higher than that of PAN and PVCH. It should be noted that the alternating, equimolar MVCH-AN copolymer has a lower thermal stability than the alternating VCH-AN copolymer (Table III, Figs. 4 and 5). The same region of decomposition is characteristic of the random VCH-AN copolymer as of PAN, but the initial rate of decomposition is lower than in the case of PAN (Fig. 5).

A distinctive feature of the thermal destruction of the random VCH-AN copolymer is that the decomposition of the copolymer is completed, as in the case of PAN, at a 50% weight loss (Fig. 5). A DTA curve presents an exo-peak in the temperature range 200–300°C. It is known that the heating of PAN is accompanied by cyclization and crosslinking. Thermal destruction of random copolymers with a higher content of AN units seems to occur according to the same mechanism as does the destruction of PAN.

Thus it can be concluded that the composition and distribution of comonomer units in copolymers of VCH and MVCH with AN exert considerable influence on their properties. The existence of strict alternation in the VCH-AN co-

TABLE III
Thermal Characteristics of Homopolymers and Copolymers of VCH and MVCH with AN

| Sample	Temperature, °C					
	In air			In argon		
	Onset of decomposition	10% weight loss	50% weight loss	Decomposition	10% weight loss	50% weight loss
PAN	130	280	440	220–560	270	560
Random VCH-AN with 75 mol % AN	230	355	460	220–550	337	420
Alternating equimolar VCH-AN	295	358	390	340–550	367	395
Alternating equimolar MVCH-AN	275	320	362	290–550	330	363
Atactic PVCH	250	310	370	330–550	347	378
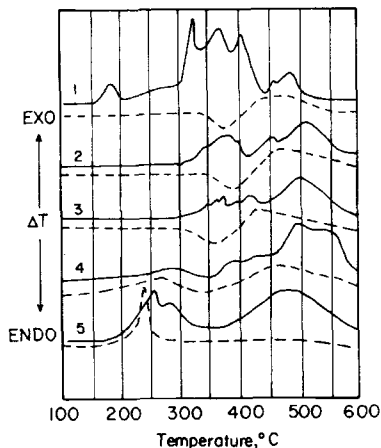
Fig. 4. DTA curves for PVCH, PAN, VCH-AN, and MVCH-AN copolymers in air (—) and argon (- - -): (1) atactic PVCH; (2) and (3) alternating, equimolar VCH-AN and MVCH-AN copolymers, respectively; (4) random VCH-AN copolymer with 75 mol % AN units; (5) PAN.
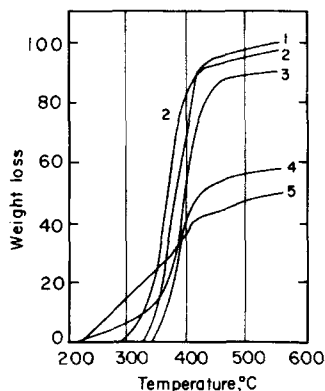

Fig. 5. Dependence of the weight loss on temperature: (1) atactic PVCH; (2) and (3) alternating, equimolar MVCH-AN and VCH-AN copolymers, respectively; (4) random VCH-AN copolymer with 75 mol % of AN units; (5) PAN. Obtained in argon.

polymers of equimolar composition results in better thermal properties as compared to the random copolymers.

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