Composition Analysis of Crosslinked Styrene–Ethylene Dimethacrylate and Styrene–Divinylbenzene Copolymers by Raman Spectroscopy

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Synopsis

A method for the determination of composition and content of pendent double bonds in untreated samples of styrene–ethylene dimethacrylate and styrene–divinylbenzene copolymers from Raman spectra has been developed. By computer treatment of spectra it was shown that Raman spectra are sensitive to the distribution of components in the studied copolymers.

INTRODUCTION

According to the classical theory of gelation in three-dimensional copolymerization of vinyl monomers, crosslinking can be interpreted as a process in which the number of branching points gradually increase up to the state of infinite network. In real systems, in addition to the formation of crosslinks, a part of the reactive vinyl groups of the crosslinking monomer is consumed in intramolecular cyclization reactions, and another part remains unreacted. In the final copolymer this latter part remains present in the form of pendent vinyl groups. A knowledge of their contents is necessary in studies of crosslinking efficiency and of the mechanism of three-dimensional polymerization in general.[1–4] The contents of pendent vinyl groups depend not only on their reactivity determined by the chemical character of the crosslinking monomer but to a large extent also on a number of physical characteristics of the polymerization process and on the properties of the polymer formed as well.

Crosslinked copolymers of vinyl monomers have found broad application as carriers of functional groups of ion exchangers and as materials for affinity chromatography, as well as sorbents in gas and liquid chromatography. High standards of reproducible quality of these materials dictated by the requirement of minimum nonspecific interaction with components of analyzed samples lead to the development of methods for the determination not only of their monomer composition but also of the functional groups present in the copolymers. Compared to other reactive groups, analysis of pendent double bonds in three-dimensional vinyl polymers has attracted relatively less attention. Their chemical determination by conventional methods of double bond analysis is complicated by the reduced reactivity of pendent vinyl groups due mainly to steric hindrance.[4–7]

Infrared spectroscopy, which is successfully used for the determination of vinyl and vinylidene groups in olefins,[8–11] in soluble three-dimensional polymers is complicated by the necessity of working in KBr pellets,[12] where the results may

be strongly affected by grinding. In homogeneous samples the content of pendent vinyl groups in styrene–ethylene dimethacrylate copolymers can be determined from near-infrared spectra.[13]

Raman spectroscopy has so far not been applied to the analysis of crosslinked styrene copolymers. As the sensitivity of this method has been recently greatly enhanced by laser excitation sources and on-line computer control, in this paper we have explored the possibilities of Raman spectroscopy in studies of styrene–ethylene dimethacrylate and styrene–divinylbenzene copolymers.

EXPERIMENTAL

Materials

Styrene. Unstabilized commercial product (Chema, n.p., Prague) was purified by vacuum distillation under nitrogen in the presence of 0.1% t-octylpyrocatechol and 0.1% Cu_2Cl_2 as polymerization inhibitors (bp 55°C/15 Torr) and further kept at temperatures below 0°C. The purity of monomers was controlled by GC (10% Ap-L/Chemosorb W 80–100; t, 120°C, N_2, 30 ml/min; injection, 0.1 μl). Content of impurities was below 1%.

Ethylene Dimethacrylate (EDMA). Product of ICI, GB. Commercial product was diluted by hexane and extracted by a 10% solution of NaOH for removal of hydroquinone type stabilizer and then by water to neutral reaction. The solution of monomer was stabilized by t-octylpyrocatechol and Cu_2Cl_2, then dried, and after evaporation of hexane vacuum distilled in nitrogen atmosphere. Boiling point 101–103°C/2 Torr. The distillate was kept at temperatures below 0°C. The purity of the distillate was determined by GC (15% Ap-L, 2% C-20M$^+$/Chromosorb W 80–100; t, 170°C; N_2, 30 ml/min; injection, 0.3 μl). Content of EDMA, 98.92%; content of polyester (hydroxyethyl methacrylate), 0.27%.

Divinylbenzene (DVB). Produced by Kaučuk n.p. Kralupy. Stabilizer from technical DVB was again removed by extraction with a 10% solution of NaOH and vacuum distilled under nitrogen in the presence of inhibitors (t-octylpyrocatechol plus Cu_2Cl_2). Boiling point 55°C/5 Torr. The distillate was kept at temperatures below 0°C. GC analysis (10% Ap-L/Chromosorb W 80–100, N_2, 30 ml/min; t, 120°C; injection, 0.1 μl): n-diethylbenzene, 0.8%; p-diethylbenzene, 0.31%; n-ethylvinylbenzene, 34.39%; p-ethylvinylbenzene, 3.16%; m-DVB, 46.56%; p-DVB, 11.86%; and 2.83% of three additional unidentified impurities.

Cyclohexanol. Produced by Lachema, n.p. Brno. Commercial product was purified only by distillation, bp 160°C/60 mm Hg. GC analysis (10% polypropylene glycol/chromosorb, t, 70°C; N_2, 30 ml/min). Purity of cyclohexanol, 99.38%.

Azobisisobutyronitrile (ABIBN). Produced by FERAK, Berlin. Was purified by crystallization from acetone at room temperature and further kept at −30°C.

Poly(vinylpyrrolidone) (PVP). Molecular weight, 750,000. Produced by BASF Ludwigshafen, BRD, trade name Luwiskol 90.

Methods

Preparation of Copolymers. All copolymers were prepared by suspension copolymerization in water. The total polymerization charge consists of the dispersion medium which in our case is always 1% aqueous solution of suspension stabilizer, i.e., PVP, and of the polymerization mixture containing the inert component (cyclohexanol), the monomer (styrene), the crosslinking agent (EDMA or DVB), and the initiator (ABIBN).

Polymerization was performed in a glass reactor with a duplicator in nitrogen atmosphere under vigorous stirring at 70°C for 15 hr. The polymerization mixture was treated by several water decantations, filtration, drying, and 8 hr of Soxhlet extraction by benzene followed by ethanol (with the exception of styrene, where the product was three times reprecipitated by methanol from $CHCl_3$ solution). The product was finally sieve fractionated and vacuum dried for 15 hr at 5 mm Hg and 80°C.

Raman Spectra. These were measured on the Coderg LRDH 800 Raman spectrometer. The spectra of the styrene–EDMA copolymers were recorded and subjected to further treatment by means of the PDP 11-05 computer. The 5145 Å filtered line of average power 600 mW produced by an argon ion laser (Coherent Radiation CR-3) was used for excitation. Spectra of the studied substances were measured in capillary cells in the 90° setting. In all measured solids, the intensity of background radiation was observed to decrease considerably with time and intensity of irradiation. Therefore, all analytically applied bands were measured after constant background intensity was reached.

RESULTS AND DISCUSSION

Analysis of Spectra of Styrene–EDMA Copolymers

In Figure 1 Raman spectra of polystyrene, poly-EDMA, and of their copolymers are shown. It is seen that the spectra exhibit bands the position of which is equal in all copolymers and the intensity of which corresponds to the molar composition. Such are for example the bands characteristic of the monosubstituted benzene ring at 622 and 1000 cm^{-1}. In all copolymers these bands are of equal width. Another analytically important band which does not change position is the band at 1732 cm^{-1}, characteristic of the carbonyl vibration. The width of this band changes linearly with molar composition of the studied copolymers.

The absolute intensity of Raman spectral lines depends not only on sample type but also on its macroscopic structure. In order to be able to compare Raman spectra of all samples, the intensities of the spectra were normalized so as to correspond to the molar composition of the sample. The maximum intensity of the band at 1000 cm^{-1} and the integrated intensity of the band at 1732 cm^{-1} were used in the normalization procedure. The spectra shown in Figure 1 have been normalized in this way. Figure 1 also contains spectra that were obtained by simple addition of spectra of polystyrene and poly-EDMA in the respective molar ratios. These "sum" spectra are seen to differ considerably from the spectra of the copolymers.

Differences between the spectra of copolymers and the "sum" spectra are relatively large for copolymers with predominating styrene units. Particularly
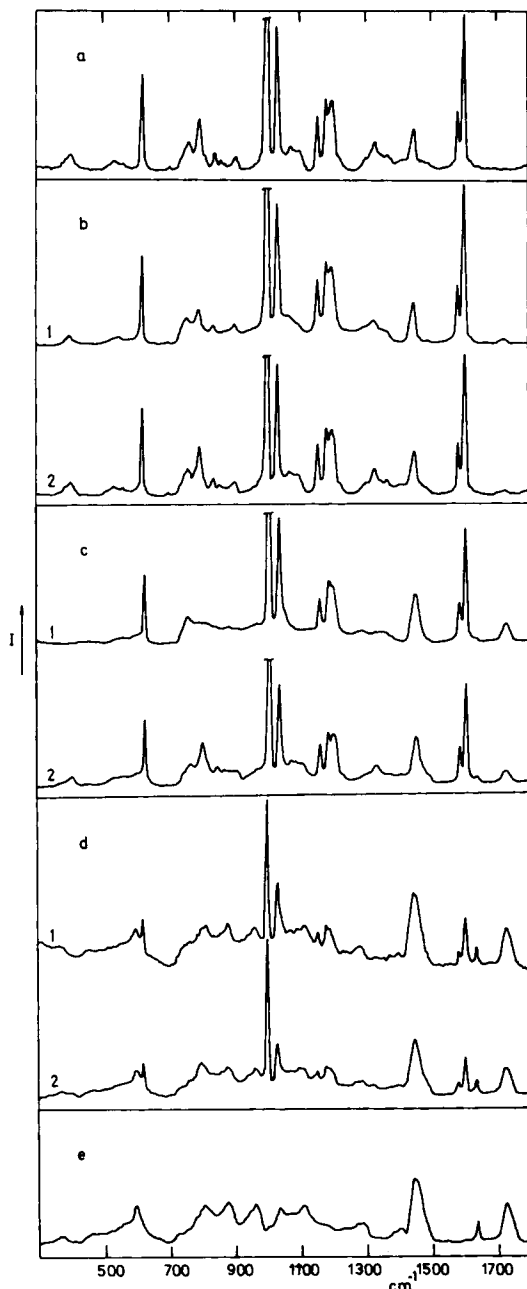
Fig. 1. Raman spectra of (a) polystyrene, (b), (c), (d) styrene–ethylene dimethacrylate copolymers, samples 4, 3, and 2, respectively; (e) poly(ethylene dimethacrylate); (1) spectra of copolymers; (2) "sum" spectra.

the intensity of bands at 795, 1070, 1100, and 1325 cm^{-1} are much lower in the spectra of copolymers than in the sum spectra. These bands evidently correspond to vibrations connected with longer sequences of styrene. Differences between the "sum" spectra and spectra of the copolymers with predominating EDMA units are relatively small. Nevertheless, the shapes of some bands are

observed to change with composition, and the band at 600 cm^{-1} is weaker in the spectra of the copolymers than in the "sum" spectra. It may be assumed that this band corresponds to a vibration connected with longer sequences of EDMA units.

As the spectra of copolymers cannot be described by the sum of the spectra of homopolymers, we have attempted to describe them as the sum of spectra of homopolymers and of an alternating copolymer, with the assumption that the copolymerization follows Bernoulli statistics. We started from sample 3, which should contain the highest amount of alternating monomer units (SE) (molar content [SE] = 0.45) in the studied series (Table I). We have approximated the spectra of sequences of two (SS) and more styrene units by the spectrum of polystyrene and the spectra of sequences of two (EE) and more EDMA units by the spectrum of poly-EDMA. We have subtracted these homopolymer spectra in amounts corresponding to SS (molar content [SS] = 0.43) and EE (molar content [EE] = 0.12) sequence contents calculated according to Bernoulli statistics from the spectrum of the sample. In this way we obtained a spectrum which should correspond to the spectrum of a hypothetical alternating copolymer. This hypothetical spectrum was then used, together with the spectra of both homopolymers, to construct spectra corresponding to the molar composition of samples 4 and 2. As the spectra constructed in this way do not differ very much from the spectra of the copolymers (Fig. 2), it is probable that the copolymerization proceeds, at least approximately, according to Bernoulli statistics.

Composition and Content of Double Bonds in Styrene–EDMA Copolymers

As the spectra of the copolymers exhibit bands the intensities of which are proportional to the content of the components, it is evident that these bands can be applied for the determination of the composition of the samples. For the determination of the content of styrene and EDMA units, the bands at 622 and at 1732 cm^{-1}, respectively, are very suitable. In the copolymers both these bands are well separated from other bands. As already mentioned, the width of the carbonyl band at 1732 cm^{-1} changes with composition, and therefore integrated intensities should be used in component analysis. As it was observed that the width of this band changes linearly with composition, the results obtained with integrated intensities do not differ from those obtained from maximum intensities. In the following calculations maximum intensities were used because these

TABLE I
Molar Composition and Contents of Double Bonds in Styrene–Ethylene Dimethacrylate Copolymers

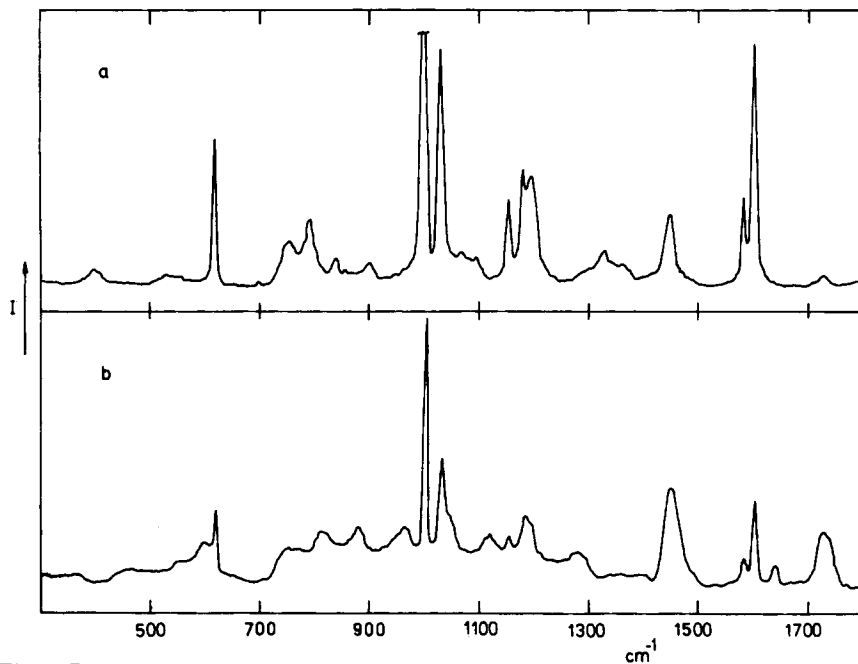| Sample	Polymerization mixture		Copolymer by spectral analysis			
	[S]	[E]	[S]	[E]	$[C_{C=C}]$	$[C_{C=C}]/[E]$
1	0	1	0	1	0.295	0.295
2	0.251	0.749	0.245	0.755	0.180	0.238
3	0.655	0.344	0.671	0.329	0.046	0.140
4	0.915	0.085	0.921	0.088	0.004	0.045
5	1	0	1	0	0	—

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Fig. 2. Raman spectra of copolymers constructed by computer assuming Bernoulli copolymerization statistics. Composition corresponding to sample 4 (a) and sample 2 (b).

are more convenient in treatment of spectra in those cases where the Raman spectrometer is not computer controlled. We have measured the intensity ratios of these bands in copolymers polymerized to 100% conversion from monomer feeds of various composition, and the results were treated by linear regression. The ratio of intensities thus obtained for I_{622}/I_{1732} is equal to 2.35. In this way we obtained an expression for the determination of the molar content of EDMA units in the copolymer:

$$[E]/[S] = 2.35(I_{1732}/I_{622})$$

where $[E]$ is the molar content of EDMA and $[S]$ is the molar content of styrene, with $[E] + [S] = 1$. The results are summarized in Table I. The mean error in the determination of $[E]$ by means of this expression is smaller than 0.008 mole, which is near to the possible error of initial monomer composition in the copolymerization. This confirms that the polymerization of our samples proceeded to full 100% conversion. In this way the composition of copolymers can be determined over the range of 85 to 5 wt. % of styrene with normal recording of Raman spectra. By accumulation of spectra with the aid of a computer this range can be further extended.

The content of unreacted double bonds can be determined by means of the band of vinyl double bonds at 1642 cm^{-1}. This band is of equal width and equal frequency in EDMA, methyl methacrylate, and the copolymers. At the same time the ratio of intensities of the double bond and the carbonyl bands, I_{1732}/I_{1642}, is equal to 0.56 both in the EDMA molecule, with two double bonds and two carbonyls, and in the methyl methacrylate molecule, with one double bond and one carbonyl. This permits us to assume that the relative intensity of the carbonyl band is equal also in the EDMA units with one or both double bonds

reacted. The molar content of the double bonds in styrene–EDMA copolymers can therefore be determined by means of the relationship

$$[C_{C=C}]/[E] = 0.56(I_{1642}/I_{1732})$$

where $[C_{C=C}]$ is the molar content of the double bonds in EDMA units. The molar contents of double bonds for our copolymer series are given in Table I and summarized in Figure 3.

Raman Spectra of Styrene–DVB Copolymers

Figure 4 shows the Raman spectra of homopolymer poly-DVB, of styrene–DVB copolymer (sample 9), of monomer styrene, and of DVB. As explained in the experimental part, the DVB used is a mixture of three substances capable of copolymerization. Due to this complication we have not attempted interpretation of the spectra. Even so, the content of double bonds can be determined also in these copolymers. For this determination use was made of the stretching vibration of vinyl double bonds which is found at 1633 cm^{-1} in styrene–DVB copolymers, in the homopolymer poly-DVB, and in monomeric styrene. As the position of this band evidently reveals equal contents of m- or p-substituted benzene rings, its intensity is probably proportional to the content of all types of unreacted double bonds. The ratio of unreacted double bonds and the content of styrene units in the copolymers can be determined directly from the observed intensity ratio of the bands at 1633 and 622 cm^{-1}. For the determination of the content of double bonds, the intensity ratio of these bands has to be known, e.g., for the case of an equal number of styrene units and once-reacted DVB units in the copolymer. As this number could not be directly determined, we have used the ratio of the intensities of these two bands in monomeric styrene, which is an approximate model for this case. In styrene the ratio of intensities of these bands $I_{1633}/I_{622} = 27$. This value was used for the determination of the contents of unreacted double bonds in the copolymers:

$$[C_{C=C}]/[D] = 0.037(I_{1633}/I_{622})$$

where $[C_{C=C}]$ is the molar content of double bonds in DVB units and $[D]$ is the molar content of DVB units. The molar content of double bonds obtained in this way is shown in Table II and in Figure 3.
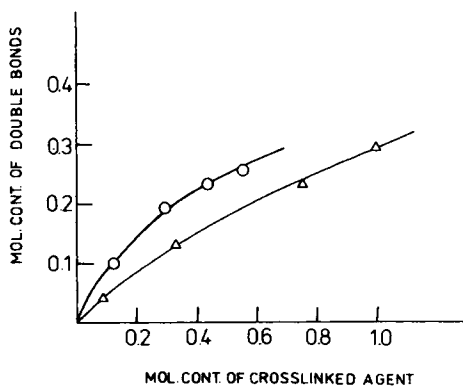

Fig. 3. Dependence of molar content of double bonds in copolymers on the molar content of crosslinking agent: (O) styrene–DVB copolymers; (△) styrene–EDMA copolymers.
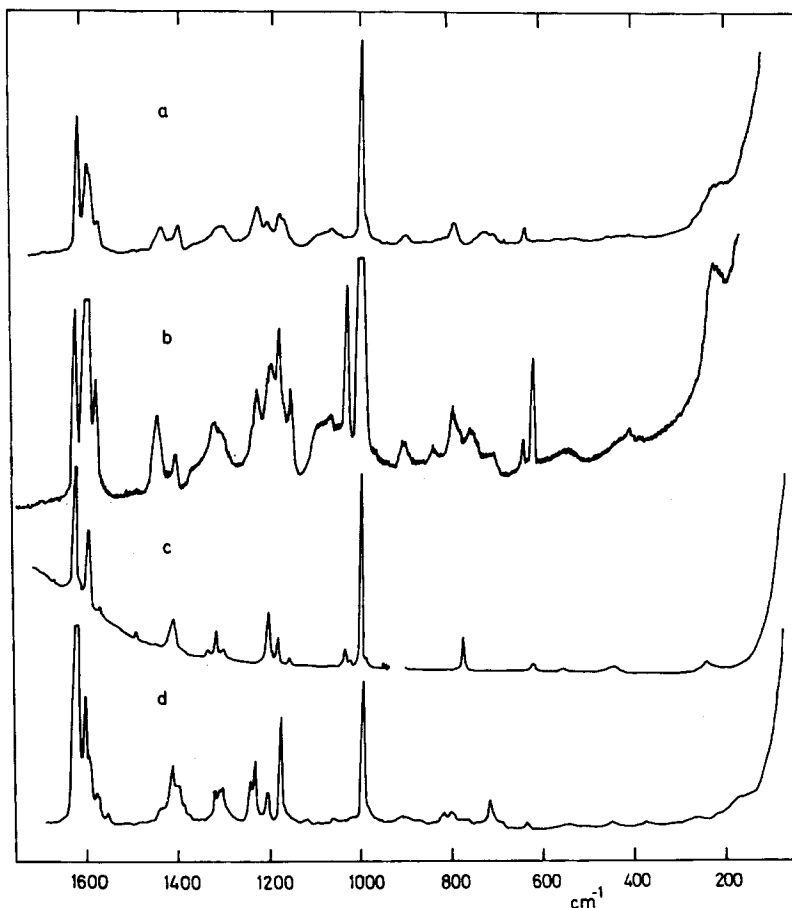
Fig. 4. Raman spectra of (a) poly-DVB; (b) copolymer styrene–DVB, sample 9; (c) styrene monomer; (d) DVB.

TABLE II
Molar Composition of Polymerization Mixture and Contents of Double Bonds in Styrene–
Divinylbenzene Copolymers

Sample	Polymerization mixture		Contents of double bonds	
	$[S]$	$[D]$	$[C_{C=C}]$	$[C_{C=C}]/[D]$
6	0	0.683	—	—
7	0.188	0.554	0.143	0.258
8	0.360	0.437	0.102	0.233
9	0.568	0.295	0.055	0.186
10	0.797	0.138	0.014	0.101
5	1	0	0	—

Tables I and II also give the relative contents of unreacted double bonds of the crosslinking agent $[C_{C=C}]/[E]$ and $[C_{C=C}]/[D]$. It is seen that the content of double bonds increases with the increasing content of crosslinking agent and that it does not differ much for the two types of comonomers. This indicates that the main reason for the appearance of unreacted double bonds in these substances is steric hindrance in the course of the crosslinking process.

To conclude, it may be stated that laser Raman spectroscopy yields in a single experiment, with very simple spectral sample preparation, data both on the composition and structure of the copolymer and on the content of pendent double bonds. Compared to other existing procedures it is considerably more precise.

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