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Investigation of the degree of crystallinity of acrylonitrile–divinylbenzene copolymers

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Using the wide-angle X-ray scattering method, the degree of crystallinity of suspension copolymers and terpolymers of acrylonitrile (AN) and divinylbenzene (DVB) were determined. Copolymers with various degrees of cross-linking (5%–50% DVB) were prepared in the presence of thermodynamically different solvents added in order to obtain porous structure. It was found that copolymers with a degree of cross-linking of 0.1% DVB have a crystallinity index below 0.2, although the crystallinity index of PAN obtained under the same conditions is 0.5. Owing to the solvation conditions, even in copolymers with a degree of cross-linking of 20% DVB, ordered regions occur, and dilution of the polymerization mixture with poor solvents cause a decrease in the degree of crystallinity of these copolymers. Terpolymers AN, butyl acrylate (BA) or vinyl acetate (VA) have less ordered structure for the same amount of DVB. Methacrylonitrile and DVB copolymers obtained under the same conditions as AN and DVB are amorphous.

1. Introduction

Although polymers and copolymers of acrylonitrile (AN) are very important commercial products of the chemical industry, there is some doubt about their physical structure. The supermolecular structure of poly(acrylonitrile) (PAN) has been the subject of many papers [1–6]. Some authors suggest a one-phase system where crystalline regions render the system heterogeneous only on a "micro"-scale [7–10]. Other authors propose a two-phase system consisting of crystalline and amorphous phases [11–14]. Differences in such models arise from the initial assumptions. Irrespective of how the number of phases in PAN is determined, most investigators agree that dipole–dipole interactions between strong nitrile polar groups and interactions between hydrogen bonds of the polymer chain and electron couples of the nitrogen atoms of the nitrile groups, are the most important in determining the structure of PAN [15–18]. The aim of the present work was to show how the degree of cross-linking and the presence of different solvents added during the suspension polymerization process effects the crystallinity (determined by the wide-angle X-ray scattering method) of cross-linked AN–DVB copolymers [19, 20].

2. Experimental procedure

The copolymers were obtained using suspension polymerization techniques. Further details on the preparation of acrylonitrile (AN) and technical divinylobenzene (DVB) copolymers and terpolymers are available elsewhere [21–26]. These compositions are coded in the sample symbols. For example HT 0.25/50 indicates that heptane (H) and toluene (T) are used; 0.25 is the initial volume fraction of monomers (AN + DVB) in the monomers and diluents mixture and 50 is the weight per cent of DVB in the monomer mixture. The degree of crystallinity was calculated using the method described by Hindeleh and Johnson [27], in which each measured profile was decomposed into the individual crystalline peaks and an amorphous halo, the decomposition of which was achieved by a least squares fit of the measured profile with the theoretically calculated curve. Wide-angle X-ray scattering (WAXS) measurements were performed using a HZG-4 diffractometer. CuK_α radiation with a wavelength of 0.154 nm was used. The radiation was monochromatized using a nickel filter and a pulse height analyser, connected to a scintillation counter. The X-ray tube was operated at 30 kV and 30 mA. WAXS patterns were taken from 5°– 40° using a step-scanning mode with a step of 0.5° and a counting time of 10 s.

3. Results

In order to estimate how the degree of cross-linking and the presence of different solvents during suspension polymerization affect the degree of crystallinity, a few series of cross-linked copolymers were synthesized

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(Tables I and II). A sample of AN (a sample HT 0.5/0) was obtained under the same conditions. The solvents were added in order to form the correct supermolecular structure of the copolymers, particularly the specific surfaces responsible for sorption properties [21–24] or to obtain porous materials useful, after modification, as carriers for biologically active substances [25, 26]. In comparison with the copolymers, linear PAN exhibits twice the crystallinity (Table I).

If the concentration of aromatic monomers of DVB and ethylostyrene is high, interaction between polar nitro groups is eliminated and copolymers become amorphous (Table I, Fig. 1a, b). From the data presented in Table I, one can conclude that the type and amount of indifferent solvents present during copolymerization of monomers affect the supermolecular structure of the copolymers. The copolymer with a degree of cross-linking of 0.2% DVB (e.g. the molar ratio of AN and aromatic monomers was 3:1) prepared in the presence of three parts by volume of a toluene–heptane mixture (9:1 vol/vol) with a solvent solubility parameter 17.9 $(\mathrm{MPa})^{1/2}$ per one part by volume of monomers, is amorphous (HT 0.25/20) (Fig. 1b). Copolymers synthesized from the same mixture of monomers but diluted only with one part by volume of solvent mixture have a degree of crystallinity equal to 13.9% (Fig. 2a). Similarly, copolymers of the HDT series with the same degree of cross-linking (20% DVB) obtained in the presence of one part by volume of a hexadecane–toluene mixture (1:9) with a solvent solubility parameter of 18.1 $(\mathrm{MPa})^{1/2}$, is crystalline. From these results it follows that long segments of AN monomers, much longer than estimated from the molar ratio, must exist in these copolymers. The calculated monomer reactivity ratio shows that in the initial stages of copolymerization, primary chains are enriched in DVB units (microgele) until the monomer is totally consumed. Then, acrylonitrile segments are produced. The presence of thermodynamically poor solvents in the polymerization system causes the polar chains to be isolated and interaction between polar groups to be broken.

All the copolymers of AN and 10% DVB (i.e. a molar ratio of AN to aromatic monomers of 10:1) are crystalline. Their crystallinity depends on the type of solvent used and falls between 13.1% and 21.1%

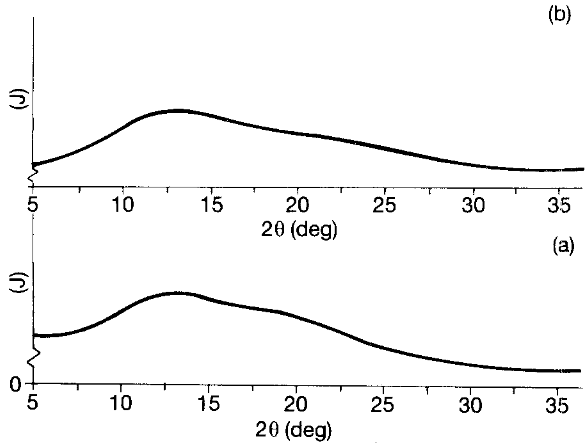

Figure 1 WAXS patterns for samples (a) HT 0.25/30, and (b) HT 0.25/20.

TABLE I Characteristics of acrylonitrile divinylbenzene copolymers

Sample[a]	Porosity	Macroporosity ($\mathrm{cm^3\,g^{-1}}$)	Surface area ($\mathrm{m^2\,g^{-1}}$)	Mean radius of pores (nm)	Degree of crystallinity (%)
HT 0.25/50	0.57	1.19	600	3.29	0.0
HT 0.25/40	0.68	1.88	430	8.51	0.0
HT 0.25/30	0.75	2.65	210	24.8	0.0
HT 0.25/20	0.72	2.24	40	110	0.0
HT 0.25/10	0.75	2.63	8	657	13.1
HT 0.25/0	0.78	3.08	200	30	50.4
10	0.26	0.39	3	260	19.4
HT 0.5/20	0.56	1.10	100	22	13.9
HT 0.5/10	0.55	1.08	40	54	19.9
HDT 0.5/20	0.54	0.96	236	8.1	8.1
HDT 0.5/10	0.57	1.14	13	175	21.1
HDT 0.5/7.5	–	–	–	–	20.2
HDT 0.5/5	–	–	–	–	19.7
HDC 0.5/10	0.53	0.98	27	72	18.5

[a] HT, heptane + toluene (1:9); HDT, hexadecane + toluene (1:9); HDC, hexadecane + cyclohexanol (1:9).

TABLE II Characteristic of acrylonitrile and divinylbenzene terpolymers

Sample	Monomers	Porosity	Macroporosity ($\mathrm{cm^3\,g^{-1}}$)	Surface area ($\mathrm{m^2\,g^{-1}}$)	Degree of crystallinity (%)
HT 0.5/10	8:1	0.58	1.17	54	15.4
HT 0.5/10	4:1	0.51	0.92	15	15.0
HDT 0.5/10	6.5:1	0.62	1.40	10	17.7
HDT 0.5/10	3:1	0.65	1.59	8	7.5
HDT 0.5/10	3:2	0.68	1.80	7	0.0

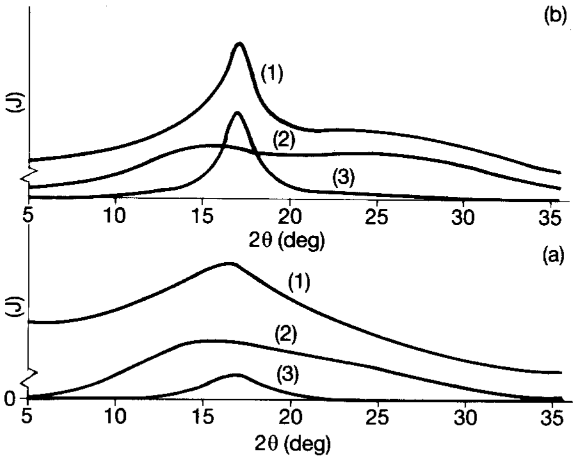

Figure 2 WAXS patterns for samples (a) HT 0.5/20, and (b) HDT 0.5/10. 1, Scattering curves; 2, amorphous haloes; 3, crystalline peaks.

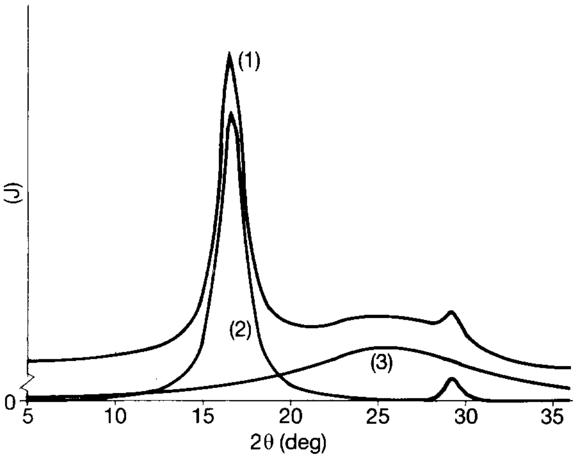

Figure 3 WAXS patterns for sample HT 0.25/10. 1, Scattering curve; 2, crystalline peak; 3, amorphous halo.

(Table I), the lowest degree of crystallinity. The copolymer HT 0.25/10, synthesized from the polymerization mixture with the highest content of indifferent solvents has the lowest degree of crystallinity (Table I, Fig. 3).

Contrary to expectation, the highest crystallinity is exibited by the copolymer obtained in the presence of a hexadecane–toluene mixture (Fig. 2b) and not by the copolymer synthesized in the presence of a thermodynamically good solvent of hexadecane and cyclohexanol (Fig. 4a, b) (solvent solubility parameter 22.7 $(\mathrm{MPa})^{1/2}$). From the previous investigations one can conclude that the copolymers described above have a significantly different supermolecular structure and, resulting from this, a ten times higher ability to absorb organic substances from water. This extremely good sorption ability can be explained by the presence of polar groups on the surface of the HDC 0.5/10 copolymer agglomerates caused by a strong interaction between nitrile groups and cyclohexanol during the copolymerization process [29].

Copolymers with the lowest degree of cross-linking (7.5% and 5% DVB) have a crystallinity similar to that of copolymers with 10% DVB.

It should be emphasized that copolymer synthesized in the absence of solvents, a so-called "gel copolymer", is also crystalline, and its degree of crystallinity does not differ significantly from that of other copolymers with 10% DVB content (sample 10, Table I, Fig. 5). The characteristics of a few cross-linked (10% DVB) terpolymers with (BA) monomers of vinyl acetate (VA) are presented in Table II. The properties of these terpolymers were described in previous papers [23, 30]. In comparison with HT 0.5/10 copolymer, terpolymer containing BA monomers exhibits a lower crystallinity.

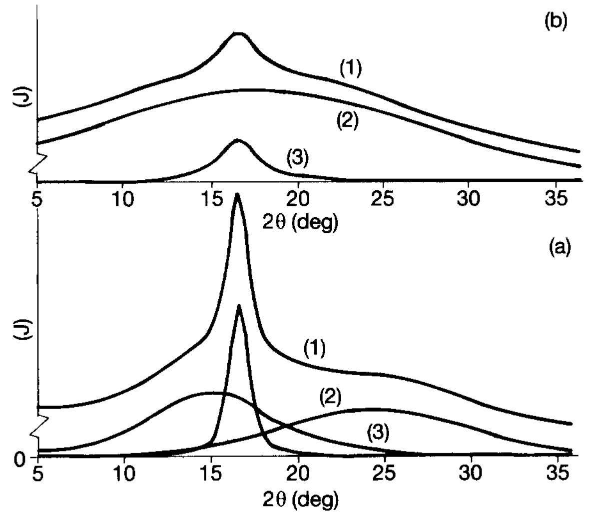

Figure 4 WAXS patterns for samples (a) HDC 0.5/10, and (b) HDT 0.5/20. 1, Scattering curves; 2, amorphous haloes; 3, crystalline peaks.

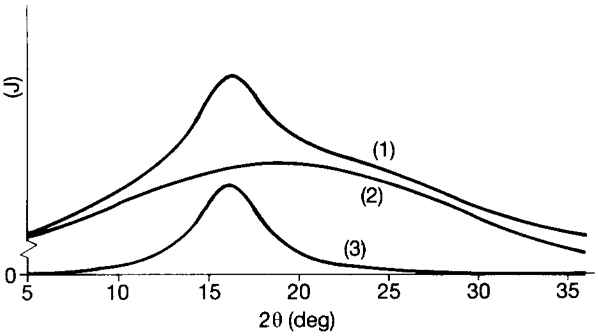

Figure 5 WAXS patterns for sample 10. 1, Scattering curve; 2, amorphous halo; 3, crystalline peak.

Vinyl acetate affects the crystallinity in proportion to its content in the terpolymers. If every 7 AN mers were randomly replaced by vinyl acetate mers, the degree of crystallinity would decrease, but if 2 of the 5 mers of AN were replaced by VA mers, amorphous terpolymers would result.

A similar decrease of crystallinity was observed in linear copolymers of AN and substituted silanes, acrylonitrile and methyl methacrylate, acrylonitrile and methacrylate of 2-hydroxyethyle copolymers [5, 31, 32].

Cross-linked copolymers of AN and DVB were compared with methacrylate and DVB. Poly(methacrylonitrile) has a well-ordered structure owing to the strong dipole–dipole interaction, but in this case hydrogen bonds are much weaker. The WAXS investigations performed showed that methacrylonitrile copolymers with a degree of cross-linking of 6%, 12% and

20% DVB, do not have crystallites detectable by this method. Further details concerning the structure and properties of methacrylonitrile copolymers will be published separately [33].

4. Conclusions

1. Cross-linked suspension copolymers of AN and DVB (10% DVB) have a crystallinity below 20%, although the crystallinity of PAN obtained under the same conditions is 50%.

2. The solvation conditions can induce ordered regions to occur, even in copolymers with 20% DVB.

3. Dilution of the polymerization mixture with poor solvents causes a decrease in the degree of crystallinity.

4. Terpolymers of AN and BA or VA have a less-ordered structure for the same amount of DVB.

5. Methacrylonitrile and divinylobenzene copolymers obtained under the same conditions as AN and DVB copolymers, are amorphous.

References

1. J. GROBELNY, P. TAKELY and E. TURSKA, *Polymer* **22** (1981) 1649.
2. J. GROBELNY, M. SOKÓŁ and E. TURSKA, *ibid.* **25** (1984) 1615.
3. P. LAGERKVIST, Dissertation, University of Geteborg (1981).
4. A. K. GUPTA, N. CHANG, R. SINGH and A. MANSINGH, *Eur. Polym. J.* **15** (1979) 129.
5. A. K. GUPTA and R.P. SINGHL *J. Polym. Sci. Polym. Phys. Ed.* **21** (1979) 129.
6 A. K. GUPTA, R.P. SINGHL and J. AGARVAL *J. Appl. Polym. Sci.* **26** (1981) 3599.
7 R. D. ANDREWS and R. M. KIMMEL, *J. Polym. Sci.* **B13** (1965) 167.
8. R. HAYAKAWA, T. NISHI, K. ARIGAWA and Y. WADE *ibid.* **A2** (1967) 165.
9. V. F. HOLLAND, A. MITCHELL, W.L. HUNTER and P. H. LINDENMEYER, *ibid.* **62** (1962) 145.
10. P. H. LINDENMEYER and R. HOSEMAN, *J. Appl. Phys.* **34** (1963) 42.
11. G. HINDRICHSEN and H. ORTH, *J. Polym. Sci. Polym. Lett. Ed.* **9** (1971) 529.
12. *Idem*, Z. KOLLOID **247** (1971) 844.
13. W. H. HOWARD, *J. Appl. Polym. Sci.* **5** (1961) 303.
14. G. HINDRICHSEN, *ibid.* **17** (1973) 3305.
15. B. G. COLVIN and P. STORR, *Eur. Polym. J.* **10** (1974) 337.
16. G. URBAŃCZYK, *Z. Nauk. Politech. Łodzkiej, Włókiennictwo*, **9** (1962) 79.
17. J. KLEMENT and P. GEIL, *J. Polym. Sci.* **A2** (1968) 1381.
18. V. F. HOLLAND *ibid.* **43** (1960) 572.
19. St. RABIEJ and A. WŁOCHOWICZ, *Angew. Makromol. Chem.* **175** (1990) 81.
20. St. RABIEJ, *Eur. Polym. J.* **27** (1991) 947.
21. M. WOJACZYŃSKA and B. N. KOLARZ, *J. Chromatog.* **358** (1986) 129.
22. B. N. KOLARZ, J. ŁUCYŃSKI, A. TROCHIMCZUK and M. WOJACZYŃSKA, *ibid.* **408** (1987) 308.
23. B. N. KOLARZ, M. WOJACZYŃSKA, A. TROCHIMCZUK and J. ŁUCZYŃSKI, *Polymer* **29** (1988) 1137.
24. A. TROCHIMCZUK and B. N. KOLARZ, *React. polym.* **11** (1989) 135.
25. B. N. KOLARZ, J. ŁOBARZEWSKI, A. TROCHIMCZUK and M. WOJACZYŃSKA *Angew. Makromol. Chem.* **171** (1989) 201.
26. B. N. KOLARZ, A. TROCHIMCZUK, J. BRYJA, M. WOJACZYŃSKA, K. DZIEGIELEWSKI and A. NOWORYTA, *ibid.* **179** (1990) 173.
27. A. M. HINDELEH and D. J. JOHNSON, *J. Polym. D Appl. Phys.* **4** (1991) 259.
28. H. H. ROSENBROCK and C. STOREY, "Computation Techniques for Chemical Engineers" (Pergamon Press, 1966).
29. M. WOJACZYŃSKA and B. N. KOLARZ, *Makromol. Chem.* in press.
30. B. N. KOLARZ, A. TROCHIMCZUK and M. WOJACZYŃSKA, *Angew. Makromol. Chem.* **193** (1991) 21.
31. L. E. WOLFRAM, J. GRASSELLI and J. L. KOENIG, *J. Appl. Spectrosc.* **24** (1970) 263.
32. A. K. GUPTA and N. CHAND, *Eur. Polym. J.* **7** (1971) 1257.
33. B. N. KOLARZ, A. TROCHIMCZUK and M. DREWNIAK, *Polymer*, in press.

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