

PRACTICAL POLYMER ANALYSIS

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PREFACE

The aim of this book is to familiarize the reader with the practical aspects of polymer analysis. A wealth of practical detail, including some detailed methods is included. The book covers not only the analysis of the main types of polymers and copolymers now in use commercially, but also the analysis of minor non-polymeric components of the polymer formulation, whether they be deliberately added, such as processing additives, or whether they occur adventitiously, such as moisture and residual monomers and solvent. A broad scheme for the examination of polymers is discussed in Chapter 2.

Practically all of the major newer analytical techniques and many of the older classical techniques, have been used to examine polymers and their additive systems. As so many different polymers are now used commercially it is also advisable when attempting to identify a polymer to classify it by first separating it into pure polymeric and gross non-polymeric fractions (Chapter 2) and then carrying out at least a qualitative elemental analysis and possible a quantitative analysis (Chapters 3 and 4) and then in some cases, depending on the elements found, to carry out functional group analysis (Chapters 6 and 9). If a simple qualitative identification of the plastic is all that is required then it is examined by finger printing techniques, as discussed in Chapter 4, in order ascertain whether a quick identification can be made by comparing its infrared or NMR spectrum, its pyrolysis-gas chromatography pattern or its thermal behaviour with those of authentic specimens of known polymers.

Frequently, however, the identification of a polymer, especially copolymers or terpolymers, is not as simple as this, and it is necessary to obtain a detailed picture of the microstructure of the polymer before an identification can be made.

Examination of polymer microstructure can be an additional means of identifying the polymer or it can be a means of helping to explain particular chemical or physical features of the polymer. In the latter case the type of polymer might already be known but we are looking for structural detail that will explain these properties such as tacticity, geometrical isomerism, regeoisomerism or the types of unsaturated structures, end-groups and branching present; (Chapter 10). In copolymers and terpolymers measurements can be made of comonomer ratio and monomer unit sequences in addition to the measurements discussed above (Chapter 9). Techniques that might be used in addition to elemental and functional group analysis, include spectroscopic techniques such as infrared, NMR, PMR, and systematic investigations by pyrolysis-gas chromatography. Examination for the type of unsaturation present, the nature of side-chain

groups and end-groups, the presence of oxygenated groups such as carbonyl and whether they are macro or micro constituents will all assist in building up a picture of the polymer structure. In many cases, considerable experience and innovative skills are required by the analyst in order to successfully identify polymers by these techniques, and it is hoped that this book will assist the analyst in developing such skills.

Examination for non-polymeric processing additives, monomers, oligomers, residual volatiles, water and catalyst remnants are discussed in Chapter 5.

In Chapter 6 is discussed the fractionation of polymers using classical techniques and more recently developed techniques such as hplc, size exclusion chromatography and supercritical fluid chromatography. Some of these techniques also provide molecular weight data which is discussed further in Chapter 7.

Other polymer physical properties which are discussed include thermal, oxidative or photo-oxidative stability, its combustion properties, measurement of glass transition temperature and other transitions, measurements of crystallinity and melting temperature and of polymer lifetimes under service conditions, (Chapters 11-13).

The book gives an up-to-date and thorough exposition of the present state of the art of polymer analysis and, as such should be of great interest to all those engaged in this subject in industry, university, research establishments and general education. It is also intended for undergraduate and graduate chemistry students and those taking courses in plastics technology, engineering chemistry, materials science and industrial chemistry. It will be useful reference work for manufacturers and users of plastics, the food and beverage packing industry, the engineering plastics industry, plastic components manufacturers, and those concerned with pharmaceuticals and cosmetics.

Before proceeding to the first two chapters, which deal respectively with the determination of elements and functional groups, it would be interest in Chapter 1 to discuss briefly the various types of polymers used commercially, and their properties and applications.

T. R. Crompton

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- Figs 1-3 Squirrel, D.C.M., Analyst (London), 106, 1042 (1981).
- Figs 5,6 Groten, B., Anal. Chem., 36, 1206 (1964).
- Fig 7 Lehman, F.F., Branch, G.M, Anal. Chem., 33, 673 (1961).
- Fig 10 Folmer, O.F. Anal. Chem, 43, 1057 (1971).
- Table 15 Juvet R.S., Smith, L.J.S., Pang, K.K., Anal. Chem., 44, 49 (1972).
- Fig 11,12 Jackson, M.T., Walker, J.Q., Anal. Chem., 43, 74 (1971).
- Table 18 Osland, R., Laboratory Practice, 37, 73 (1971).
- Fig 13 Brako, F.D., Wexler, A., Anal. Chem., 35, 1944 (1963).
- Tables 19,20 Dobies, R.S.J., Chromatography, 40, 110 (1969).
- Figs 14,15 &
Table 15 Schabon, J.T., Fenska, L.E., Anal. Chem., 52, 1411 (1980).
- Figs 16,17 &
Table 23 Albarino, R.V., Applied Spectroscopy, 27, 47 (1973)
- Fig 18 Soncek, J., Jelinova, E., Analyst (London), 107, 623 (1982).
- Fig 19 Drushel, H.V., Sommers, A.L., Anal. Chem., 36, 836 (1964).
- Fig 21 Krisher, A., Anal. Chem., 43, 1130 (1971).
- Table 27 Simpson, D., Currell, B.R., Analyst (London), 96, 515 (1971).
- Tables 29 & 43 Millingen, M.B., Anal. Chem., 46, 746 (1974).

- Table 32 Robertson, M.M., Rowley, R.M., British Plastics, 26
January (1960).
- Fig 22 Majors, R.E.J., Chromatographic Science, 8, 338 (1970).
- Table 36 Denning, J.A., Marshall, J.A., Analyst (London), 97 710
(1972).
- Table 37 Lappin, G.R., Zannucci, J., Anal. Chem., 41, 2076
(1976).
- Fig 23 Tittarelli, P., Zerlia, T., Colli, A. and Ferrari, G.,
Anal. Chem., 55, 220 (1983).
- Table 41 Protivova, J., Posposil, S.J., Chromatography, 88, 99
(1974).
- Fig 24 Anderson, D.M.W., Analyst (London), 84, 50 (1959).
- Fig 25(a) &
Table 45 Cambell, R.H., Wize, R.W., J. Chromatography, 12, 178
(1963).
- Fig 25(b) Schabaum, J.F., Fenska, L.E., Anal. Chem., 52, 1411
(1980).
- Fig 26 &
Table 46 Vargo, J.D., Olsen, K.L., Anal. Chem., 57, 672 (1985).
- Figs 27,28 McCoy, R.N., Fiebig, E.C., Anal. Chem., 37, 593 (1965).
- Figs 29-31 &
Table 49 Juvet, R.S., Smith, L.S., and Li, K.P., Anal. Chem., 44,
49 (1972).
- Tables 56,57 Striechen, R.J., Anal. Chem., 48, 1398 (1976).
- Fig 36 &
Table 58 Betso, S.R., McLean, J.D., Anal. Chem., 48, 766 (1976).
- Table 59 Skelly, N.E., Husser, E.R., Anal. Chem., 50, 1959
(1978).
- Fig 40 Roper, J.N., Anal. Chem., 42, 688 (1970).
- Figs 43,44 Jeffs, A.R., Analyst (London), 94, 249 (1969).
- Table 66 Korenaga, T., Analyst (London), 106, 40 (1981).
- Table 73 Baltiste, D.R., Butler, J.P., Cross, J.B., McDaniel,
M.P., Anal. Chem., 53, 2232 (1981).
- Table 74 Hyden, S., Anal. Chem., 35, 133 (1963).
- Fig 45 Brako, F.D., Wexler, A.S., Anal. Chem., 35, 1944 (1963).
- Table 75 Stelzer, R.S., Smullin, C.F., Anal. Chem., 34, 194
(1962).

- Table 76 Smith, R.M., Dauson, M., Analyst (London), 105, 85 (1980).
- Fig 46 &
Table 77 Ho, F.T., Anal. Chem., 45, 603 (1973).
- Table 78 Kim, C.S.Y., Dodge, A.I., Hay, S., Kawasaki, A., Anal. Chem., 54, 232 (1982).
- Table 79 Schleuter, D.D., Siggia, S.S., 49, 2343 (1977).
- Fig 47 Fletcher, J.P., Persinger, H.E., J. Polymer Science, A-1, 6, 1025 (1968).
- Fig 48
Tables 81-83 Mori, S., Uno, Y., Anal. Chem., 59, 90 (1987).
- Table 84 Atkinson, E.R., Calouche A., Anal. Chem., 43, 460 (1971).
- Figs 49-51 Mourney, T.H., Smith, G.A., Snyder, L.R., Anal. Chem., 56 1774 (1984).
- Figs 52-53 Mourney, T.H., Anal. Chem., 56, 1777 (1984).
- Fig 54 &
Table 85 Bode, R.K., Benningfidd, L.V., Mowrey, R.A., Fuller, E.N., International Laboratory, 40, Nov/Dec (1981).
- Fig 55 &
Tables 87-91 Mori, S., Anal. Chem., 53, 1813 (1981).
- Fig 56 &
Table 92 Mori, S., Anal. Chem., 55, 2414 (1983).
- Fig 57 Tally, C.P., Bowman, L.M., Anal. Chem., 51, 2239 (1979).
- Fig 58-61 &
Table 93 Mori, S., Uno, Y., Suzuki, M., Anal. Chem., 58, 303 (1986).
- Fig 62 Williamson, G.R., Cervenka, A., European Polymer Journal, 8, 1009 (1972).
- Fig 66 Taylor, W.C., Tung, L.H., Paper presented at 140th Meeting of American Chemical Society, Chigaco, Illinois, September (1961).
- Fig 67, 68 Machtie, W., Klodwig, H., Mackromal Chem., 180, 2507 (1979).
- Table 94 Williamson, G.R., Cervenka, A., European Polymer Journal, 10, 295 (1974).
- Table 95 Lattimer, R.P., Harmon, D.J., Houson, G.E., Anal. Chem., 52, 1808 (1980).

- Fig 7 &
Tables 105,106 Van Houwlinger, G.D.B., Analyst (London), 106, 1057 (1981).
- Table 100 Altenau, H.G., Headley, L.M., Jones, S.O., Rensaw, H.C., Anal. Chem., 42, 1280 (1970).
- Table 101 Anderson, D.G., Isakson, K.E., Snow, D.L., Tessari, D.J., Vandenberg, J.T., Anal. Chem., 43, 894 (1971).
- Table 102 Barrall, B.M., Porter, R.S., Johnson, D.E., Anal. Chem., 35, 73 (1963).
- Fig 72 Porter, R.S., Nickosic, S.W. and Johnson, J.F., Anal. Chem., 35 1948 (1963).
- Table 103 Van Lingen, R.L.M., Fresenius, Z., Anal. Chem., 169, 410 (1969).
- Figs 73,74 Douglas, J., Timnick, A. & Guile, R.L., J. Polymer Science, A-1, 1609 (1963).
- Fig 75 &
Table 104 Johnson, D.E., Lyeria, J.R., Horikawa, T.T., & Pederson, L.A., Anal. Chem., 77, 49 (1977).
- Fig 76 Sharp, J.L. & Patenson, G., Anal. Chem., 105, 517 (1980).
- Fig 77 &
Table 108 Anderson, D.G., Isakson, K.E., Vandenberg, J.T., Jao, M.Y.T., Tessari, D.J. & Afremow, L.C., Anal. Chem., 47 1008 (1975).
- Fig 78 Tsuji, K. & Kouishi, K., Analyst (London), 99 54 (1974).
- Fig 79 &
Table 109 Swaraj, S., Ranby, B., Anal. Chem., 47, 1428 (1975).
- Fig 80 Peltonen, K., Pfaffi, P. & Itkonen, A., Analyst (London), 110, 1173 (1985).
- Fig 81
Tables 110-112 Hammerich, A.D. & Willeboodse, F.G., Anal. Chem., 45, 1696 (1973).
- Fig 82 &
Tables 113-115 Schleuter, D.D., Siggia, S., Anal. Chem., 49 2349 (1977).
- Fig 83 Tukuchi, T., Tauge, S. & Sigimura, Y., J. Polymer Science, A-1, 6, 3415 (1968).
- Table 116 Krishen, A., Anal. Chem., 44, 494 (1972).
- Fig 84 &
Table 117 Tosi, G., Simonazzi, T., Die Augewandte Makromolecular Chemie, 32, 153 (1973).

- Fig 85 Drushell, H.V., Iddings, F.A., Division of Polymer Chemistry, 142nd Meeting American Chemical Society, Atlantic City, September (1962).
- Tables 118,119 Lomonte, J.N, Tirpak, G.A., J. Polymer Science, A2, 705 (1964).
- Fig 86 & Table 120 Brown, J.E., Tyron, M. & Mandel, J., Anal. Chem., 35, 2173 (1963).
- Table 121 Paxton, J.R., Randall, J.C., Anal. Chem., 50, 1777 (1978).
- Figure 87 Neumann, E.W., Nadeau, H.G., Anal. Chem., 10, 1454 (1963).
- Table 122,123 Anderson, D.G., Isakson, K.E., Snow, D.L., Tessari, D.J., Candleberg, J.T., Anal. Chem., 43, 894 (1971).
- Fig 88 & Table 125 Allen, B.J., Elsea, G.M., Keller, K.P., Kinder, H.D., Anal. Chem., 49, 471 (1977).
- Fig 89 & Table 126 Brame, E.G., Yeager, F.W., Anal. Chem., 48, 709 (1976).
- Fig 90 & Table 127 Blackwell, J.T., Anal. Chem., 48, 1883 (1976).
- Fig 91 & Table 129 Voigt, J., Kunststoffe, 54, 2 (1964).
- Fig 92 Van Schooten, J., Evenhuis, J.K., Polymer (London), 6, 651 (1965).
- Fig 93-95 Lehmann, F.A., Brauer, G.M., Anal. Chem., 33, 676 (1961).
- Fig 96 Van Schooten, J., Evenhuis, J.K., Shell Chemical Co., Holland, private communication.
- Tables 131,132 Bucci, G., Simmonazzi, T., J. Polymer Science, C-7, 203 (1964).
- Fig 97 & Table 133 Van Schooten, J., Duck, E.W., Berkenbosch, R., Polymer (London), 2, 357 (1961).
- Fig 98 Veerkamp, M.A., Veermans, A., Makromol. Chemie, 50, 147 (1961).
- Fig 99 Porter, R.S., J. Polymer Science, A1, 4, 189 (1966).
- Table 134 Paxton, J.R., Randall, J.C., Anal. Chem., 50, 1777 (1978).
- Figs 100-102 & Tables 137,138 Sugimura, Y., Takenchi, T., Anal. Chem., 50, 1173 (1978).

- Table 141 Porter, R.S., J. Polymer Science, A-1, 4, 189 (1966).
- Fig 106 Randall, J.C., J. Polymer Science, 13, 889 (1975).
- Fig 107 Binder, J.L., J. Polymer Science, A1, 42 (1963).
- Table 143,144 Carlson, D.W., Ransaw, H.C., Altenau, A.G., Anal. Chem., 42 1278 (1970).
- Tables 147-149 Vodchnal, J., Kossler, I., Coll. of Czech. Commun. 29, 2428, 2859 (1964).
- Fig 110 Luongo, J.P., Salovay, R., J. Applied Polymer Science, 7, 2307 (1963).
- Fig 114 O'Mara, H.M., J. Applied Polymer Science, A-1, 8, 1887 (1970).
- Tables 157-159 Van Schooten, J., Evenhuis, J., Polymer (London), 6, 651 (1965).
- Fig 115 Seger, M., Barrall, E., J. Polymer Science, A-1, 13, 1515 (1975).
- Table 160 Ahlstrom, D.H., Liebman, S.A., Abbass. J. Polymer Science, Polymer Chemistry Edition, 14, 2479 (1976).
- Figs 124-127 Kullik, E., Kaljurand, M. & Lainberg, M., Laboratory Practice, p73, Jan-Feb (1987).
- Fig 128 &
Tables 165,166 Shulman, G.P., Polymer Letters, 3, 911 (1965).
- Figs 129,130,
133,144 &
Tables 167,168 Risby, T.H., Yergey, J.A., Anal. Chem., 54, 2228 (1982).
- Figs 131-132 &
Tables 169-171 Undseth, H.R., Friedman, L., Anal. Chem., 53, 29 (1981).
- Table 174 O'Mara, M.M., J. Polymer Science, A-1, 8, 1887 (1970).
- Figs 135-138 &
Tables 175,176 Chang, T.L., Head, T.E., Anal. Chem., 43, 534 (1971).
- Fig 139 Peltonen, K., Analyst (London), 111, 819 (1986).
- Fig 144 Schole, R.G., Bednarczyk, J., Yamanchi, T., Anal. Chem., 38, 331 (1966).
- Fig 146 Joseph, K.T., Browner, R.E., Anal. Chem., 52, 1083 (1980).
- Figs 151,152 Wohitjen, H., Dessy, K., Anal. Chem., 51, 1470 (1979).
- Fig 153 Wohitjen, H., Dessy, K., Anal. Chem., 51, 1463 (1979).

- Figs 173,174 &
Table 188 Bergmann, K., Polymer Bulletin, 5, 355 (1981).
- Figs 176,177 Young, P.H., Spectroscopy International, 1, 50 (1989).
- Fig 178 Clappett, B.H., Anal. Chem., 35, 1834 (1963).
- Fig 181 Illers, K.H., Heckmann, W., Hambrecht, J., Colloid and
Polymer Science, 262, 557 (1984).
- Fig 182 Simack, P., Makromal Chemie, 178, 2927 (1977).

CONTENTS

CHAPTER 1 TYPES OF POLYMERS AND THEIR USES	1
CHAPTER 2 POLYMER CHARACTERISTICS REQUIRING ELUCIDATION	10
2.1 Identification of Unknown Polymers (10)	
2.2 Microstructure (15)	
2.3 Other Physical Properties (15)	
CHAPTER 3 SEPARATION OF POLYMER AND ADDITIVES	16
3.1 Introductory (16)	
3.2 Fractional Precipitation (16)	
3.3 Fractional Extraction (17)	
3.4 Diffusion Methods (17)	
3.5 Dialysis or Electrodialysis (17)	
3.6 Practical Examples (17)	
3.6.1 Polyolefins (23)	
3.6.2 Polystyrene (27)	
3.6.3 Acrylics (27)	
3.6.4 PVC (28)	
3.6.5 Rubbers (30)	
3.6.6 Polyacrylamide (30)	
3.6.7 Polyurethane (30)	
3.6.8 Copolymers (30)	
CHAPTER 4 IDENTIFICATION OF POLYMERS	32
4.1 Introductory (32)	
4.2 Simple Physical Tests (32)	
4.2.1 Solvent solubility (33)	
4.2.2 Ignition tests (33)	
4.2.3 Colour reactions (34)	
4.2.4 Qualitative elemental analysis (34)	
4.3 Quantitative Elemental Analysis (46)	
4.3.1 Chlorine, bromine, iodine (46)	
4.3.2 Fluorine (54)	
4.3.3 Sulphur (55)	
4.3.4 Nitrogen (60)	
4.3.5 Phosphorus (68)	
4.4 Fingerprinting Techniques (72)	
4.4.1 Introductory (72)	
4.4.2 Thermal analysis techniques (72)	
4.4.3 Pyrolysis techniques (73)	

- 4.4.4 Photolysis - gas chromatography (87)
- 4.4.5 Pyrolysis - mass spectrometry (89)
- 4.4.6 Infrared spectroscopy (92)
- 4.4.7 Raman spectroscopy (103)
- 4.4.8 NMR and PMR spectroscopy (105)

CHAPTER 5 ADDITIVES, VOLATILES AND CATALYST REMNANTS

106

- 5.1 Additives (106)
 - 5.1.1 Introductory (106)
 - 5.1.2 Phenolic antioxidants (108)
 - 5.1.3 Amine antioxidants (126)
 - 5.1.4 Phenolic/amine types (127)
 - 5.1.5 Dialkyl thiodipropionates (139)
 - 5.1.6 Tertiary phosphites (142)
 - 5.1.7 Plasticizers (143)
 - 5.1.8 Ultraviolet absorbers (148)
 - 5.1.9 Organotin stabilizers (155)
 - 5.1.10 Metal stearate and other types of stabilizers (160)
 - 5.1.11 Organic and inorganic pigments (160)
 - 5.1.12 Flame retardants (163)
 - 5.1.13 Organic peroxides (163)
 - 5.1.14 Antiozonants (164)
 - 5.1.15 Rubber accelerators (165)
 - 5.1.16 Mixtures of additives (167)
- 5.2 Monomers and Oligomers (194)
 - 5.2.1 Styrene and alpha-methyl styrene in polystyrene (194)
 - 5.2.2 Styrene and acrylonitrile (202)
 - 5.2.3 Vinyl chloride, butadiene, acrylonitrile, styrene and 2-ethylhexyl acrylate (203)
 - 5.2.4 Acrylic acid and acrylamide (206)
 - 5.2.5 Other monomers (209)
 - 5.2.6 Oligomers (209)
- 5.3 Residual Volatiles (210)
 - 5.3.1 Introductory (210)
 - 5.3.2 Expanding agents in polystyrene (solution analysis) (211)
 - 5.3.3 Aromatics in polystyrene (solution analysis) (212)
 - 5.3.4 Aliphatics in polyolefins (213)
 - 5.3.5 Aromatics in polystyrene (head space analysis) (217)
 - 5.3.6 Diaminotoluenes in polyurethanes (219)
 - 5.3.7 Other volatiles (221)
- 5.4 Water (221)
 - 5.4.1 Polyolefins, vinyls and acrylics (221)
 - 5.4.2 Polyesters (223)
 - 5.4.3 Other polymers (225)
- 5.5 Catalyst Remnants (225)
 - 5.5.1 Introductory (225)
 - 5.5.2 Trace metals (226)
 - 5.5.3 Trace halogens (230)
 - 5.5.4 Trace sulphur (233)
 - 5.5.5 Trace phosphorus (233)
 - 5.5.6 Trace nitrogen (233)
 - 5.5.7 Other trace elements (234)
 - 5.5.8 Non-destructive techniques (234)
 - 5.5.9 Trace organic peroxide residues (238)

CHAPTER 6 FUNCTIONAL GROUPS IN POLYMERS

241

- 6.1 Introductory (241)
- 6.2 Unsaturation (241)
- 6.3 Hydroxy Groups (244)
- 6.4 Carboxyl Groups (251)
- 6.5 Carbonyl Groups (251)
- 6.6 Other Oxygenated Groups (252)
- 6.7 Alkyl and Aryl Groups (253)
- 6.8 Total Silanol, Silane Hydrogen Groups and Tetrapropoxy Silane and Diphenyl Silane Cross-linking Agents (254)
- 6.9 Amino Groups (255)
- 6.10 Nitric Ester Groups (255)
- 6.11 Nitrile Groups (255)

CHAPTER 7 FRACTIONATION OF POLYMERS

256

- 7.1 Introductory (256)
- 7.2 Grosslinked Gel Content (257)
- 7.3 Gradient Elution Techniques (258)
- 7.4 Precipitation Techniques (259)
- 7.5 Thin-Layer and Paper Chromatography (259)
- 7.6 Gas Chromatography (259)
- 7.7 Liquid Chromatography (260)
 - 7.7.1 HPLC (260)
 - 7.7.2 Size exclusion chromatography (274)
 - 7.7.3 Supercritical fluid chromatography (300)

CHAPTER 8 MOLECULAR WEIGHT

304

- 8.1 Introductory (304)
- 8.2 Absolute Weight Average Molecular Weight, (M_w) (305)
 - 8.2.1 Light scattering (305)
 - 8.2.2 Sedimentation (307)
 - 8.2.3 Size exclusion chromatography (307)
- 8.3 Absolute Number Average Molecular Weight, (M_n) (308)
 - 8.3.1 Osmometry (308)
 - 8.3.2 End-group analysis (310)
- 8.4 Viscosity Average Molecular Weight, (M_v) (313)
- 8.5 Field Desorption Mass Spectrometry (315)
- 8.6 NMR Spectroscopy (321)

CHAPTER 9 COPOLYMER COMPOSITION

322

- 9.1 Introductory (322)
- 9.2 Functional Group Analysis (322)
 - 9.2.1 Unsaturation (322)
 - 9.2.2 Diene groups in ethylene-propylene-diene terpolymers (327)
 - 9.2.3 Ester groups (330)
 - 9.2.4 Carboxyl groups (339)
 - 9.2.5 Carbonyl groups (348)
 - 9.2.6 Hydroxyl groups (348)
 - 9.2.7 Alkoxy groups (352)
 - 9.2.8 Oxyalkylene groups (356)
 - 9.2.9 Epoxy groups (360)
 - 9.2.10 Anhydride groups (367)

- 9.2.11 Amino groups (368)
- 9.2.12 Amido and imido groups (369)
- 9.2.13 Nitrile groups (375)
- 9.3 Comonomer Contents and Ratios (376)
 - 9.3.1 Acrylonitrile-butadiene-styrene terpolymers (377)
 - 9.3.2 Natural rubber, styrene-butadiene rubber and ethylene-propylene-diene elastomer in cured stocks (377)
 - 9.3.3 Ethylene and propylene units in ethylene-propylene copolymers (378)
 - 9.3.4 Butene-1 units in ethylene-butene copolymers (388)
 - 9.3.5 Styrene and acrylate units in styrene-acrylate copolymers (389)
 - 9.3.6 Methacrylate and styrene units in styrene-methacrylate copolymers (391)
 - 9.3.7 Ethylene glycol, 1,4-butane diol, terephthalic and isophthalic acids repeat units in Terylene (393)
 - 9.3.8 Hexafluoropropylene and vinylidene fluoride repeat units in hexafluoropropylene-vinylidene fluoride copolymer (397)
 - 9.3.9 Monomer units in other olefin copolymers (400)
- 9.4 Monomer Unit Sequence Determination in Copolymers (400)
 - 9.4.1 Introductory (400)
 - 9.4.2 Sequencing in ethylene-propylene copolymers (400)
 - 9.4.3 Sequences in polyethylene (424)
 - 9.4.4 Sequences in polypropylene (427)
 - 9.4.5 Sequences in polyisoprene (427)
 - 9.4.6 Sequences in butadiene-propylene copolymers (429)
 - 9.4.7 Sequences in ethylene-methyl methacrylate random copolymers (430)
 - 9.4.8 Sequence in other Polymers (436)

CHAPTER 10 POLYMER MICROSTRUCTURE

437

- 10.1 Introductory (437)
- 10.2 Stereoisomers and Tacticity (438)
 - 10.2.1 Polypropylene (439)
 - 10.2.2 PVC (448)
 - 10.2.3 Other polymers (449)
- 10.3 Geometrical Isomers (452)
 - 10.3.1 Polybutadiene (452)
 - 10.3.2 Polyisoprene (457)
- 10.4 Regioisomerism (465)
 - 10.4.1 Introductory (465)
 - 10.4.2 Polypropylene (466)
 - 10.4.3 Ethylene-propylene copolymers (469)
 - 10.4.4 Polybutene-1-ethylene copolymers (472)
 - 10.4.5 Poly 2,3 dimethyl butadiene (472)
 - 10.4.6 Polybutadiene (472)
 - 10.4.7 Polyisoprene (474)
 - 10.4.8 Polypropylene glycols (476)
 - 10.4.9 Other polymers (478)
- 10.5 Forms of Unsaturation in Polyolefins and Other Polymers (478)
 - 10.5.1 Polyethylene (478)
 - 10.5.2 Polypropylene (481)
 - 10.5.3 Other polymers (484)
- 10.6 Short Chain Branching (484)
 - 10.6.1 Polyethylene (484)
 - 10.6.2 Polybutene-1 (491)
 - 10.6.3 Ethylene-higher olefin copolymers (491)
 - 10.6.4 PVC (498)

CHAPTER 11 THERMAL, OXIDATIVE AND PHOTOSTABILITY

506

- 11.1 Thermal Stability (506)
 - 11.1.1 Introductory (506)
 - 11.1.2 Thermal analysis techniques (507)
 - 11.1.3 Applications, thermogravimetric analysis (508)
 - 11.1.4 Applications, differential thermal analysis (518)
 - 11.1.5 Applications, differential scanning calorimetry (518)
 - 11.1.6 Applications, thermal volatilization analysis (519)
 - 11.1.7 Applications, evolved gas analysis (520)
 - 11.1.8 Thermal analysis equipment (561)
- 11.2 Oxidative Stability (571)
 - 11.2.1 Thermal methods (571)
 - 11.2.2 Infrared spectroscopy (579)
 - 11.2.3 Electron spin resonance spectroscopy (582)
- 11.3 Photooxidative Stability (582)
- 11.4 Examination of Polymer Combustion Products (585)
- 11.5 Combustion Testing (587)
 - 11.5.1 Introductory (587)
 - 11.5.2 Mining applications (589)
 - 11.5.3 Electrical applications (589)
 - 11.5.4 Transportation applications (590)
 - 11.5.5 Furniture and fittings applications (591)
 - 11.5.6 Construction material applications (592)
 - 11.5.7 Other fire-related factors (593)

CHAPTER 12 GLASS TRANSITION TEMPERATURE AND OTHER TRANSITIONS 595

- 12.1 Introductory (595)
- 12.2 T_g by Differential Thermal Analysis (595)
- 12.3 T_g by Differential Scanning Calorimetry (596)
- 12.4 T_g and Other Transitions by Thermomechanical Analysis (597)
- 12.5 T_g by Dynamic Mechanical Analysis (608)
- 12.6 T_g and other Transitions by Spectroscopy (608)
- 12.7 Applications of Dynamic Mechanical Analysis (608)
 - 12.7.1 Characterization of viscoelastic and rheological properties (608)
 - 12.7.2 T_g Measurement (615)
 - 12.7.3 Alpha, beta and gamma transition measurement (617)
 - 12.7.4 Prediction of polymer lifetime (620)

CHAPTER 13 DEGREE OF CRYSTALLINITY AND MELTING TEMPERATURE 630

- 13.1 Degree of Crystallinity (630)
 - 13.1.1 Introductory (630)
 - 13.1.2 Thermal methods (630)
 - 13.1.3 NMR spectroscopy (631)
 - 13.1.4 Infrared spectroscopy (634)
 - 13.1.5 X-ray diffraction (636)
 - 13.1.6 X-ray diffraction/infrared microscopy (636)
- 13.2 Measurement of Crystallization Phenomena (639)
 - 13.2.1 Thermal methods (639)
 - 13.2.2 Spectroscopic methods (644)
- 13.3 Melting Temperature, T_m (644)
 - 13.3.1 Thermal methods (644)