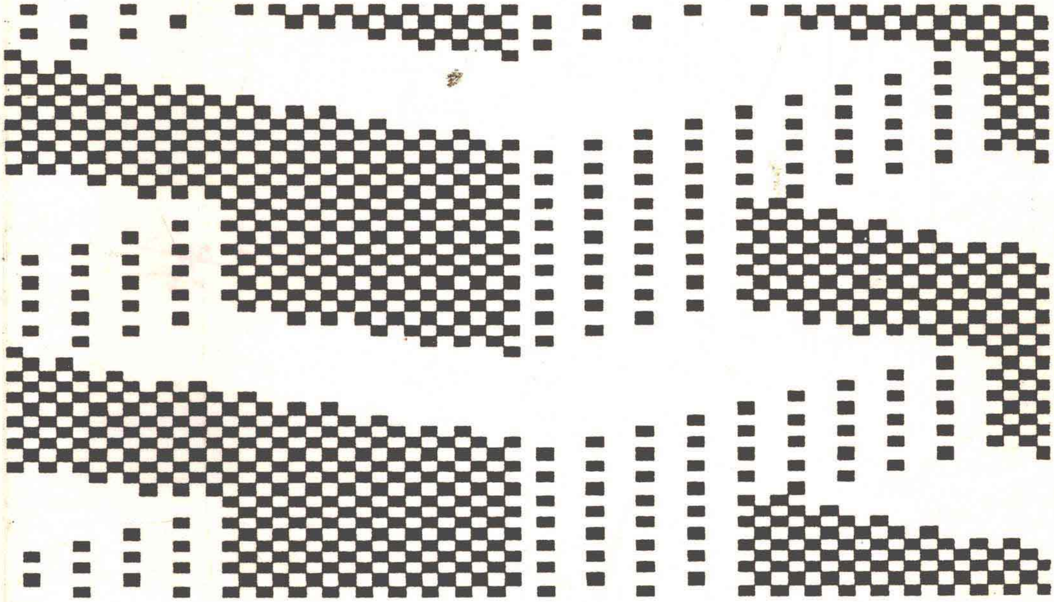
POLYMERS
AN INTRODUCTION



T. R. CROMPTON

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Analysis of Polymers

AN INTRODUCTION

by

T. R. CROMPTON

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Analysis of Polymers

AN INTRODUCTION

Preface

The aim of this book is to familiarize the reader with all aspects of plastic analysis. The book covers not only the analysis of the main types of plastics now in use commercially, but also the analysis of minor non-polymeric components of the plastics formulation, whether they be deliberately added, such as processing additives, or whether they occur adventitiously, such as moisture and residual monomers and solvents.

Practically all of the major newer analytical techniques, and many of the older classical techniques, have been used to examine plastics 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 carrying out at least a qualitative elemental analysis and possibly a quantitative analysis (Chapter 2) and then in some cases, depending on the elements found, to carry out functional group analysis (Chapter 3). If a simple qualitative identification of the plastic is all that is required then it is examined by fingerprinting techniques, as discussed in Chapter 4, in order to ascertain whether a quick identification can be made by comparing its infrared spectrum and pyrolysis–gas chromatography pattern 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 identification can be made (Chapter 5). 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.

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 a 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 of interest in Chapter 1 to discuss briefly the various types of polymers used commercially, and their properties and applications.

Contents

1

Types and properties of polymers

SYNTHETIC resins, in which plastics are also included, vary widely in their chemical composition and in their physical properties. The number of synthetic resins which can be made is vast; relatively few, however, have achieved commercial importance.

Well over 90% of all synthetic resins made today comprise no more than 20 different types, although there are certain variations to be found within each type. Synthetic resins are familiar to most people as plastics, but they have other uses, such as in the manufacture of surface coatings, glues, synthetic textile fibres, etc. The rapid growth of the synthetic resin industry has to a large extent been made possible by the fact that ample supplies of the necessary raw materials have become available from petroleum.

The synthetic resins may be divided into two classes, known respectively as 'thermosetting' and 'thermoplastic' resins, each class differing in its behaviour on being heated. The former do not soften; the latter soften, but regain their rigidity on cooling. Both types are composed of large molecules, known as macromolecules, but the difference in thermal behaviour is due to differences in internal structure.

The large molecules of the thermoplastics have a long-chain structure, with little branching. They do not link with each other chemically, although they may intertwine and form a cohesive mass with properties ranging from those of hard solids to those of soft pliable materials, in certain cases resembling rubber. On being heated, the chain molecules can move more or less freely relative to each other, so that, without melting, the material softens and can flow under pressure and be moulded to any shape. On cooling, the moulded articles regain rigidity. Some resins require the addition of liquid plasticizers to improve the flow of the plastic material in the mould. In such cases the moulded articles are usually softer and more flexible than the products made from the unplasticized resins.

The macromolecules of the thermosetting resins are often strongly-branched chains and are chemically joined by crosslinks, thus forming a complex network. On heating, there is less possibility of free movement, so that the material remains rigid.

Production of synthetic resins

Production of these resins also falls into two groups since there are, generally, two main types of chemical reaction by which they are made. These are polycondensation reactions and polymerization reactions.

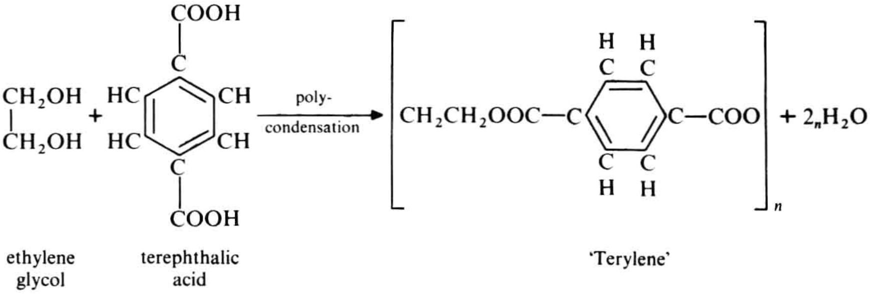
Polycondensation reactions

In this type of reaction two or more chemicals are brought together and a reaction between them is initiated by using heat or a catalyst or both. The reaction proceeds with the elimination of water and the molecules are joined by chemical bonds to form macromolecules, either long-chain or crosslinked structures of the thermoplastic or thermosetting types, respectively. Many resins obtained by polycondensation are the thermosetting type.

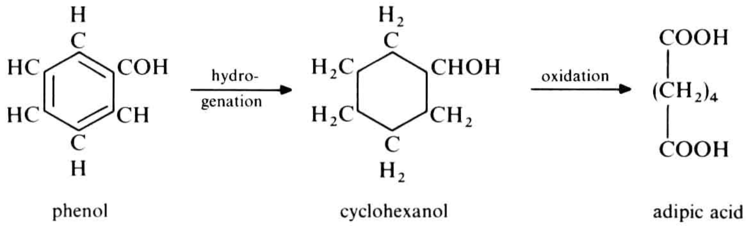
In the manufacture of these resins the chemical reactions are arrested at an intermediate stage in which the resins are temporarily thermoplastic; they are set in their final shape by the application of heat and pressure. At this stage the interlinking of the molecules takes place.

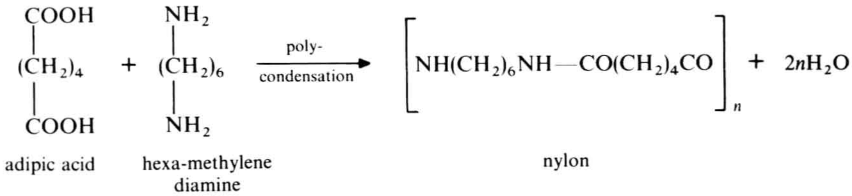
Important thermosetting synthetic resins made by polycondensation, using petroleum chemicals as raw materials, include the phenol-formaldehyde ('Bakelite'), urea-formaldehyde, alkyd- and epoxy- types.

Resins with long-chain macromolecules obtained by polycondensation have thermoplastic properties. Polyesters ('Terylene') and polyamides (nylon) are examples of polycondensations. The synthetic fibre 'Terylene' (known as 'Dacron' in the U.S.A.) is a polyester formed by the reaction of ethylene glycol with terephthalic acid; the terephthalic acid is obtained from paraxylene by oxidation.



Nylon type fibres (polyamides) are manufactured from adipic acid, which can be made from either cyclohexane or phenol. The adipic acid is condensed with hexa-methylene diamine, which is a derivative of adipic acid.





$$\underset{\text{adipic acid}}{\begin{array}{c}COOH\\|\\(CH_2)_4\\|\\COOH\end{array}} + \underset{\text{hexa-methylene diamine}}{\begin{array}{c}NH_2\\|\\(CH_2)_6\\|\\NH_2\end{array}} \xrightarrow[\text{condensation}]{\text{poly-}} \underset{\text{nylon}}{\left[NH(CH_2)_6NH{-}CO(CH_2)_4CO\right]_n} + 2nH_2O$$

Polymerization reactions

Resins produced by polymerization reactions, known technically as high polymers, are rapidly increasing in number and in importance as compared with the polycondensation resins. High polymers are usually made by joining together into long chains a number of molecules which have the same kind of reactive points or groupings in their structure. These individual molecules are usually olefins or other compounds with double bonds, and are called ‘monomers’. The molecule of the polymer often contains hundreds of monomer units.

The manufacture of high polymers therefore takes place in two stages: first, the production of the monomer, or repeating chemical unit; and second, the polymerization to a resin.

Thus, if we take the preparation of polyvinyl chloride as an example we have:

1st Stage

$$\underset{\text{ethylene}}{CH_2{=}CH_2} + \underset{\text{chlorine}}{Cl_2} \rightarrow \underset{\substack{\text{dichloro}\\\text{ethane}}}{CH_2Cl{-}CH_2Cl} \rightarrow \underset{\substack{\text{vinyl chloride}\\\text{(monomer)}}}{CH_2{=}CHCl} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{HCl}$$

2nd Stage

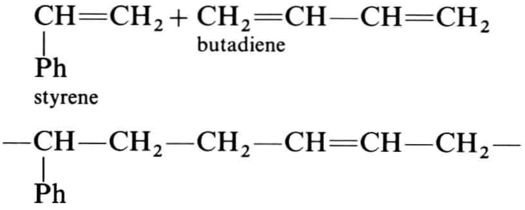
$$\underset{n\text{ molecules vinyl chloride}}{CH_2{=}CHCl + CH_2{=}CHCl + CH_2{=}CHCl + \cdots} \xrightarrow{\text{polymerization}}$$

$$\underset{\text{polyvinyl chloride}}{{-}CH_2CHCl{-}CH_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2CHCl{-}}$$

In some cases it is possible to form polymers from two or even three monomers which may differ from one another in chemical form and yet be capable of linking end-to-end to form mixed monomer chains. These are known as 'copolymers', and such polymers form the basis of the most important types of synthetic rubber.

Further examples of polymerizations:

Styrene butadiene copolymer

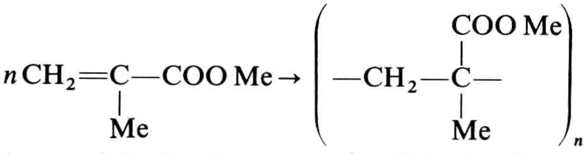


$$\underset{\text{styrene}}{\underset{\displaystyle Ph}{\overset{|}{CH}}{=}CH_2} + \underset{\text{butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

$$-\underset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-CH_2-CH{=}CH-CH_2-$$

styrene–butadiene copolymers

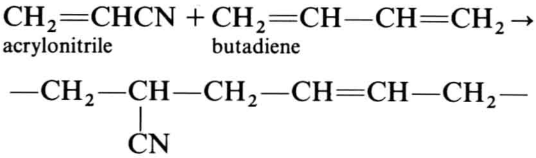
Polymethylmethacrylate



$$n\,CH_2{=}\underset{\displaystyle Me}{\overset{|}{C}}-COO\,Me \rightarrow \left(-CH_2-\underset{\displaystyle Me}{\overset{|}{\overset{\displaystyle COO\,Me}{C}}}-\right)_n$$

methylmethacrylate polymethylmethacrylate

Buna N rubber



$$\underset{\text{acrylonitrile}}{CH_2{=}CHCN} + \underset{\text{butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \rightarrow$$

$$-CH_2-\underset{\displaystyle CN}{\overset{|}{CH}}-CH_2-CH{=}CH-CH_2-$$

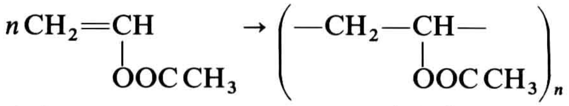
acrylonitrile–butadiene copolymer

Vinyl chloride–vinylidene chloride copolymers

$$\underset{\text{vinyl chloride}}{CH_2{=}CH{-}Cl} + \underset{\text{vinylidene chloride}}{CH_2{=}CCl_2} \rightarrow$$

$$-CH_2-CCl_2-CH_2-CHCl-$$

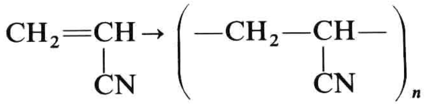
Polyvinylacetate



$$n\,CH_2{=}\underset{\displaystyle OOC\,CH_3}{\overset{|}{CH}} \rightarrow \left(-CH_2-\underset{\displaystyle OOC\,CH_3}{\overset{|}{CH}}-\right)_n$$

vinyl acetate polyvinylacetate

Polyacrylonitrile

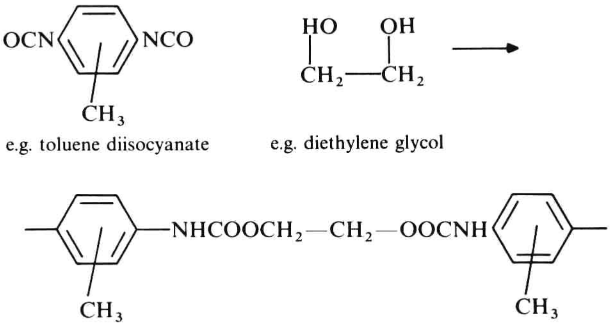


$$CH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} \rightarrow \left(-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}- \right)_n$$

acrylonitrile

polyacrylonitrile (Orlon Acrilan)

Polyurethanes



e.g. toluene diisocyanate

e.g. diethylene glycol

Numerous high molecular weight polymers are produced commercially. The properties and some of the uses of these are discussed below under separate headings. Many more copolymers exist than polymers and many, but not all, of these are produced in relatively small quantities for more specialized applications. Some of the more important copolymers are included; mechanical, physical, electrical and chemical properties of the important commercially produced polymers are compared in Table 1. Data on the properties of metals are included for comparison. Table 2 tabulates some of the uses to which these plastics are put.

TABLE 1 *Physical and chemical properties of polymers*

	Specific gravity ASTM D 792	Impact strength ASTM D 256 (J/12.7 mm)	Tensile strength ASTM D 638,651 (MN m^{-2})	Elongation in tension ASTM D 638 (%)	Modulus of elasticity in tension ASTM D 747 (MN m^{-2} × 10^{-2})	Flexural strength ASTM D 790 (MN m^{-2})	Compressive strength ASTM D 695 (MN m^{-2})
Polycondensation types							
Phenol formaldehyde							
(a) Unfilled	1.25–1.3	0.13–0.24	48–55.3	1.0–1.5	51.8–69	83.9–103.6	69–203
(b) Woodflour/cotton flock filled	1.32–1.45	0.16–0.4	44.9–58.8	0.4–0.8	55.3–83.9	58.8–83.9	152–276
Urea formaldehyde							
Cellulose filled	1.47–1.52	0.17–0.24	41.4–89.7	0.5–1.0	104	69–110.5	172–241
Melamine formaldehyde							
(a) Unfilled	1.48	—	—	—	—	76–96.6	276–311
(b) α-cellulose filled	1.47–1.52	0.16–0.24	48–89.7	0.6–0.9	89.7	69–110.5	172–297
Polyesters							
(a) Resin	1.1–1.4	0.5	42–91	1.5–2.5	—	59–152	91–280
(b) Dough moulding compound	1.7–2.3	1.4–2.3	28–70	—	—	84–140	140–210
(c) Sheet moulding compound	1.7–2.6	7.0–10.0	56–140	—	—	67–172	105–210
Epoxides							
(a) Rigid	1.0–3.2	0.2–0.62	34.5–83.9	5–10	13.8–41.4	69–138	104–203
(b) Flexible	1.2	0.43–1.02	6.9–27.6	10–100	—	20.3–69	—
Nylons							
(a) Type 6	1.13	0.68–2.45	70.5–83.9	90–320	10.4–24.8	55.3–110.5	48.4–96.6
(b) Type 6/6	1.14	0.68–1.36	48–83.9	60–300	17.9–27.6	55.3–95.3	48.4–110.5
(c) Type 11	1.04–1.05	1.2	55–60	300–350	—	69.0	55
(d) Type 12	1.01–1.02	1.4	55	150–300	—	73.5	—
Polymerization types							
Polyethylenes							
(a) Low density	0.91–0.93	No Break	6.9–15.9	90–650	1.18–2.42	No Break	Excessive cold flow
(b) High density	0.941–0.965	1.02–8.15	21.4–38	50–800	5.53–10.4	13.8–20.3	16.5
Polypropylene	0.9–0.91	0.27–4.25	29–38	50–600	8.92–13.8	34.5–55	58.8–69

Polystyrenes							
(a) Conventional	1.04–1.11	0.13–0.34	34.5–83.9	1.0–2.5	27.6–41.4	83.9–117.5	79.4–110
(b) Toughened	0.98–1.1	0.27–2.05	17.2–48	7–60	17.2–31	27.6–69	27.6–62.2
Styrene acrylonitrile	1.075–1.1	0.24–0.34	65.7–83.9	1.5–3.5	27.6–38.7	96.6–131	96.6–117
Acrylonitrile/buta-diene/styrene	0.99–1.1	2.04–8.15	17.2–62	10–140	6.9–28.3	24.8–93.2	17.2–76
vinyl polymers							
(a) Rigid polyvinyl chloride	1.38–1.4	0.68–2.04	58.8	2–40	24.2	93.2	55.3
(b) Rigid vinyl chloride/vinyl acetate	1.37–1.45	0.34–0.68	51.9–58.8	200–450	↕	83.9	—
(c) Rubber modified PVC	1.35	10.2 (Unaged)	41.4	—	41.4	83.9	89.7
Polyacetals	1.425	1.56 extrusion 0.95 injection	69	15 injection 75 extrusion	28.3	97.4	ca 124
Polycarbonates	1.2	8.15–10.7	58.8–65.7	60–100	22	76–89.7	76
Ionomers	0.93–0.96	—	28–35	—	1.8–2.1	2100	—
Polyphenylene oxide	1.06–1.1	1.5	50–65	20–60	—	90–95	102–104
Polyphenylene sulphide	1.6–1.9	—	74–131	0.5–1.25	—	102–185	70–145
Acrylics	1.17–1.2	0.2–0.43	48–76	3–10	31	89.7–117.5	83.9–138
Ethylene vinylacetate	0.925–0.95	No Break	10–18	750–900	—	20–26	—
Fluorinated polymers							
(a) Fluorinated Ethylene Propylene	2.14–2.17	No Break	17.2–24.2	—	3.45–4.8	11.05	19.7
(b) Polytetrafluoroethylene	2.1–2.2	1.70–2.72	17.2–41.1	250–600	3.45–6.22	No Break	4.84–12.4
(c) Polytrifluorochloroethyelene	2.1–2.15	1.70–2.45	31.8–39.4	125–175	13.1–20.3	24.1	13.8
Cellulosic plastics							
(a) Cellulose acetate	1.23–1.34	0.27–3.53	13.1–58.8	6–70	4.49–27.6	13.8–110.5	15.2–248
(b) Cellulose acetate butyrate	1.15–1.22	0.54–4.27	17.9–47.7	40–90	3.45–13.8	12.4–64.3	14.5–152
(c) Cellulose propionate	1.18–1.24	0.43–6.78	13.8–50.5	30–100	4.14–14.8	26.9–76	21.4–152
Metals and alloys							
(a) Brass (Cu-Zn, 70/30)	8.5	45.8	320	65–70	965*	—	—
(b) Mild steel (0.6% Carbon)	7.87	24	459	45	2030*	—	760–897
(c) Carbon steel (0.4% Carbon)	7.85	3.4	505	28	2000*	—	ca 1360
(d) Aluminium (99% Pure)	2.82	13.5	83.9	15–30	710*	—	—
(e) Duralumin (Al-Si-Cu-Mg)	2.8	Variable	247	25–29	690*	—	—
(f) Phosphor bronze (Cu-Sn-P)	8.98	Variable	402	15	1100*	—	—

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*Calculated from tensile strength and elongation data

TABLE 1 *Contd.*

	Hardness (Rockwell) ASTM D 785	Dissipation (power) factor ASTM D 150 (10^6 Hz)	Dielectric constant ASTM D 150 (10^6 Hz)	Dielectric strength ASTM D 149 (Short time 0.125″ thick V mm^{-1} × 10^{-2})	Volume resistivity ASTM D 257 (Ohm cm^{-1} at 23°C and 50% RH)	Thermal. expansion ASTM D 696 (mm mm^{-1} °C^{-1} × 10^{-5})	Specific heat (kJ kg^{-1})
Phenol formaldehyde							
(a) Unfilled	M124–M128	0.015–0.03	4.5–5.0	118–158	10^{11}–10^{12}	2.5–6	1.6–1.76
(b) Woodflour/cotton flock filled	M100–M120	0.03–0.07	4.0–7.0	79–168	10^{9}–10^{13}	3–4.5	1.45–1.68
Urea formaldehyde							
Cellulose filled	M115–M120	0.25–0.35	6.4–6.9	118–158	10^{12}–10^{13}	2.7	1.68
Melamine formaldehyde							
(a) Unfilled	—	—	—	—	—	—	—
(b) α-Cellulose filled	M110–M125	0.027–0.045	7.2–8.2	118–158	10^{12}–10^{14}	4	1.68
Polyesters							
(a) Resin	—	0.006–0.026	2.8–4.1	132–200	10^{13}–10^{16}	5.5–10	—
(b) Dough moulding compound	—	0.007–0.02	5.2–6.4	136–168	10^{14}–10^{15}	1.1–5	1.04
(c) Sheet moulding compound	—	0.015–0.024	4.2–5.8	152–180	10^{14}–10^{16}	2	1.04
Epoxides							
(a) Rigid	—	0.01–0.02	3.0–4.0	138–177	$> 10^{15}$	5–9	—
(b) Flexible	—	0.01–0.02	3.0–4.0	118–158	$> 10^{15}$	5–9	—
Nylons							
(a) Type 6	R103–R118	0.02–0.13	3.0–7.0	173–201	10^{12}–10^{15}	8–13	1.68
(b) Type 6/6	R108–R118	0.02–0.06	3.6–6.0	152–185	0.45–4×10^{14}	10–15	1.68
(c) Type 11	R108	0.011–0.022	3.2	168	4.3×10^{13}	15	2.4
(d) Type 12	R106	0.03	3.1	180	2.5×10^{15}	10.4	2.1
Polymerization types							
Polyethylenes							
(a) Low density	D41–D46 (Shore)	< 0.0005	2.25–2.35	181–276	$> 10^{16}$	16–18	2.3
(b) High density	D60–D70 (Shore)	< 0.0003	2.25–2.35	> 316	$> 10^{16}$	11–13	2.22–2.3
Polypropylene	R85–R110	0.0002–0.0003	2.25–2.3	> 316	$> 10^{16}$	11	1.93