Articles Figures Tables About A graft copolymer has a backbone consisting of one type of monomer and branches of another (Fig. 3.9). For example, high impact polystyrene is formed from a polystyrene backbone with grafted polybutadiene branches. [Pg.30] Graft copolymers are commonly produced by building reactive sites into a iinear polymer. Then in a subsequent reaction, polymerization by the comonomer is carried out at these reactive sites. For example, the incorporation of random vinyi bromide units in poiystyrene provides sites for subsequent production of a graft poiystyrene-poiymethyi methacrylate copolymer. [Pg.31] Graft copolymers are also formed by radical and ionic processes [262, 263, 284-286], They are usually difficult to characterize, and their synthesis is poorly reproducible. [Pg.336] As with block copolymers, to describe their synthesis would require an extensive treatise. In principle they can be formed by some variant of the following processes [Pg.337] Preparation of graft copolymers by chain biting reactions [Pg.337] Carbanions can react with Cl in PVC macromolecules [295] and with the ester group of PMMA [284]. The rates of the two reactions are probably not very different by the addition of a-methylstyrene tetramer dianion to a PVC + PMMA solution, the copolymer poly(vinyl chloride)-gro/ir-poly-(methyl methacrylate) was obtained [296]. Macrocations formed by the reaction of strong acids with polyalkenes (see Chap. 3, Sect. 3.2) react with polyethers (polysiloxanes) yielding graft and block copolymers, e. g. poly(propylene)-0ra/ir-poly (oxyethylene) [297], poly(propylene)- /ocA - [Pg.337] These reactions are just an example of many other possibilities since a backbone substituent, or the chain backbone directly is attacked, I propose to call these processes chain biting reactions. [Pg.338] Graft copolymers should in principle exhibit similar structure/properties relationships as block copolymers. The problem is that pure graft copolymers which are not accompanied by large amounts of homopolymers are - with few exceptions - very difficult to synthesize. This is the reason why reliable property [Pg.142] Although copolymers with equivalent eom-positions but different molecular architec- [Pg.190] As shown in Eq. (35), graft copolymers containing a mesogenic monomer have been synthesized by free radical copolymer- [Pg.190] Entry (Number average) block length PMMA LC Wt. ratio PMMA/LC Thermotropic behavior ( ) Weighted average s Tg (°C) [Pg.191] Comparison of the data in Tables 14 and 19 of graft and block copolymers, respectively, based on methyl methacrylate and a mesogenic methacrylate confirm that block copolymers phase separate more easily than graft copolymers. Although not exactly comparable due to the different mesogenic methacrylates, the block copolymers phase separate at shorter block lengths than the graft copolymers. In addition, the distribu- [Pg.191] III Molecular Engineering of Side Chain Liquid Crystalline Polymers [Pg.192] Synthesis of graft copolymers resembles that of block copolymers with an increased number of reactive sites per macromolecule. There are two techniques similar to those used in block copolymer preparation, namely grafting from and grafting onto preformed chains. Another method, grafting through, is similar to that used in conventional random copolymerization, where in-chain units function as comonomers. [Pg.287] Block copolymers are linear, but graft copolymers are branched, with the main chain generally consisting of a homopolymer or a random copolymer, while the grafted side chains are composed of either the same or another monomer or several monomers [Pg.256] The numerous ways for the synthesis of graft copolymers can be divided into three categories. [Pg.257] To the first category belong the homo- and copolymerization of macromonomers. For this purpose, macromolecules with only one polymerizable end group are needed. Such macromonomers are made, for example, by anionic polymerization where the reactive chain end is modified with a reactive vinyl monomer. Also methacrylic acid esters of long-chain aliphatic alcohols or monofunctional polyethylene oxides or polytetrahydrofurane belong to the class of macromonomers. [Pg.257] The second possible route is called grafting from . This means that active sites are generated at the polymer backbone A which initiate the polymerization of monomer B, thus leading to long-chain branches [Pg.258] CHjCl or nitroxy group (controlled radical polymerization), [Pg.258] Three methods exist for synthesizing graft copolymers. Grafting onto involves the reaction between functional groups on two different polymers [Pg.752] Grafting from involves a polymer with functional groups that initiate polymerization of [Pg.753] Grafting through involves the polymerization (or copolymerization) of a macromonomer, usually a vinyl macromonomer [Pg.753] SCCO2 from P(HEMA-co-PMMA) did not occur from all of the hydroxyl groups on the polymeric initiator. In all cases, steric effects were suggested to be responsible for the incomplete grafting reaction [116]. [Pg.393] A surface-initiated enzymatic ROP has also been reported, whereby CL and DXO were grafted from hydroxyl-terminated self-assembled monolayers (SAMs) on gold, using Novozym 435 [117], while polycaprolactone-modified hydroxyethylcel-lulose films were prepared by the enzymatic ROP of CL [118]. [Pg.393] Ckinventional free-radical polymerization, either by so-called graffing-ffom or grafting-onto techniques are the oldest and were the most widely used procedures for the synthesis of graft copolymers because they are very simple [2]. In fact, graft copolymers can easily be obtained by polymerization of a monomer A in presence of a preformed polymer B acting, either as a chain-transfer agent or as a macroinitiator. However, these procedures usually [Pg.184] PEC methacrylic macromonomer PLA methacrylic macromonomer POE methacrylic macromonomer [Pg.186] Adapted and completed from Ref.]15], Copyright 2003, with permission from Elsevier. [Pg.186] A first improvement, as shown by Rempp and Merrill [109] was the grafting-onto by ionic polymerization techniques as for instance for the preparation of amphiphilic PS-g-PEO graft copolymers. Such copolymers were obtained by deactivation of a living PEO, of known molecular weight, on a partially chloromethylated PS backbone. [Pg.188] In the case of composites, the surface modification leads to a good dispersion of the inorganic material in polymers matrices and, depending on the nature of the dispersed phase, imparts improved chemical and physical properties such as mechanical properties, UV attenuation, flame retardancy, thermal stability, thermal and electrical conductivity, gas barrier properties, superhydrophobicity, antimicrobial properties, etc. [Pg.207] The functionalization or modification of the particle surface with chemical groups or polymer grafts is the key to achieve excellent dispersion in polymer matrices and [Pg.207] The modification of polymers can be readily conducted by chemical coupling reactions when the chain to be modified possesses groups such as vinyl, hydroxyl, or azide [23], etc. The Diels-Alder reaction between a diene and a dienophile, discovered by Otto Diels and Kurt Alder in 1928 [24], is the most important example of click chemistry. These robust and efficient click coupling reactions have been widely exploited in the construction of tailor-made functional polymeric materials with complex molecular architectures [Pg.207] The production of thermoplastics by polymer grafting synthesis techniques is widely used in the industry today. Large amounts of commercial thermoplastics, especially styrenic polymers, are nowadays produced by diverse grafting techniques, but other graft polymers are also produced commercially. Some of the most relevant examples are discussed below. [Pg.207] 1 High Impact Polystyrene (HIPS) HIPS is a heterogeneous material produced by continuous bulk or bulk-suspension processes, in which a butadiene-based elastomer (polybutadiene (PB), or a block copolymer of styrene-butadiene) is first dissolved in styrene monomer (St) and the resulting mixture is then heated so that the polymerization proceeds either thermally or with the aid of a chemical initiator. At the molecular level, the product is a mixture of free polystyrene (PSt) chains and elastomer chains grafted with PSt side chains. The process yields a continuous (free) PSt matrix containing [Pg.207] The extent of the cross-linking, as shown above, is not clear. It is known, however, that cleavage reactions that are followed by free-radical recombinations can take place [274] [Pg.617] Polymeric chains bearing free radicals combine with each other to give branched structures. Additions of chains with freeradical to double bonds result in formations of cross-links [274], [Pg.617] Many other miscellaneous cross-Unkings of pol5mieric materials are reported in the literature. For instance, poly(acryloyl chloride) can be cross-linked with diamines [275] [Pg.617] In a similar manner, polymers with pendant chlorosulfonate groups cross-link when reacted with diamines or with glycols [275]. [Pg.617] This is an important part of polymer syntheses that is used in many industrial processes. In 1967, Battaerd and Tregear [282] published a book on the subject that contains 1,000 references to journal publications and 1,200 references to patents. In addition, there are several monographs and many review papers [283]. The synthetic methods developed to date range from using free radical attacks on polymeric backbones to highly refined ionic reactions. There are examples where these ionic reactions attach the side-chains at well-designated locations. [Pg.617] In graft copolymers the chain backbone is composed of one kind of monomer and the branches are made up of another kind of monomer. [Pg.1007] Remember from Sec. 1.3 that graft copolymers have polymeric side chains which differ in the nature of the repeat unit from the backbone. These can be prepared by introducing a prepolymerized sample of the backbone polymer into a reactive mixture—i.e., one containing a source of free radicals—of the side-chain monomer. As an example, consider introducing polybutadiene into a reactive mixture of styrene ... [Pg.394] Figure 9.17 Plot of log [i]M versus retention volume for various polymers, showing how different systems are represented by a single calibration curve when data are represented in this manner. The polymers used include linear and branched polystyrene, poly(methyl methacrylate), poly(vinyl chloride), poly(phenyl siloxane), polybutadiene, and branched, block, and graft copolymers of styrene and methyl methacrylate. [From Z. Grubisec, P. Rempp, and H. Benoit, Polym. Lett. 5 753 (1967), used with permission of Wiley.]... Solution polymers are the second most important use for acryflc monomers, accounting for about 12% of the monomer consumption. The major end use for these polymers is in coatings, primarily industrial finishes. Other uses of acryflc monomers include graft copolymers, suspension polymers, and radiation curable inks and coatings. [Pg.171] Monomer compositional drifts may also occur due to preferential solution of the styrene in the mbber phase or solution of the acrylonitrile in the aqueous phase (72). In emulsion systems, mbber particle size may also influence graft stmcture so that the number of graft chains per unit of mbber particle surface area tends to remain constant (73). Factors affecting the distribution (eg, core-sheU vs "wart-like" morphologies) of the grafted copolymer on the mbber particle surface have been studied in emulsion systems (74). Effects due to preferential solvation of the initiator by the polybutadiene have been described (75,76). [Pg.203] In addition to graft copolymer attached to the mbber particle surface, the formation of styrene—acrylonitrile copolymer occluded within the mbber particle may occur. The mechanism and extent of occluded polymer formation depends on the manufacturing process. The factors affecting occlusion formation in bulk (77) and emulsion processes (78) have been described. The use of block copolymers of styrene and butadiene in bulk systems can control particle size and give rise to unusual particle morphologies (eg, coil, rod, capsule, cellular) (77). [Pg.204] M. G. Huguet andT. R. Paxton, Colloidal andMorphological Behavior of Block and Graft Copolymers Plenum, New York, 1971,pp. 183—192. [Pg.208] Material Protection. The graft copolymers of ethylene sulfide on polyethyleneimine can be used as an antifouHng anticorrosion substrate for iron (439). PEIs or their derivatives are also used in electrolysis baths as brighteners in the electrochemical deposition of metals (440,441). [Pg.13] In addition to providing fully alkyl/aryl-substituted polyphosphasenes, the versatility of the process in Figure 2 has allowed the preparation of various functionalized polymers and copolymers. Thus the monomer (10) can be derivatized via deprotonation—substitution, when a P-methyl (or P—CH2—) group is present, to provide new phosphoranimines some of which, in turn, serve as precursors to new polymers (64). In the same vein, polymers containing a P—CH group, for example, poly(methylphenylphosphazene), can also be derivatized by deprotonation—substitution reactions without chain scission. This has produced a number of functionalized polymers (64,71—73), including water-soluble carboxylate salts (11), as well as graft copolymers with styrene (74) and with dimethylsiloxane (12) (75). [Pg.259] H. A. J. Battaerd and G. W. Tregear, Polymer Reriem, Graft Copolymers, Vol. 16, Wiley-Interscience, New York, 1967. [Pg.272] A hydrolyzed cereal soHd, predominately a hexasaccharide, is used in high pH lime muds for reducing the yield point and gel strength (67). This additive has been used in systems treated with both sodium hydroxide and potassium hydroxide in addition to other additives common to lime muds (68). A second viscosity-reducing additive used in lime muds is a graft copolymer of acryflc acid and calcium flgnosulfonate (69). Both of these materials are used at levels of 6—17 kg/m (2—6 lb /bbl). [Pg.180] Acrylamide graft copolymers such as those with starch (qv)(131), dextran (132), and lignin (qv) (133), have been studied to try to reduce copolymer costs. A general disadvantage of acrylamide copolymers is greater cost compared to partially hydroly2ed polyacrylamides. [Pg.192] Grafting can also occur in the amide nitrogen, either through an anionic-type mechanism which is beheved to operate when ethylene oxide [75-21 -8] and similar copolymers are grafted to polyamides, or through a polycondensation mechanism when secondary amides are formed as graft copolymers (70). [Pg.226] Fig. 6. Illustration of (a) compatibiLization of immiscible blends of polymers and B by block or graft copolymers and (b) the subsequent modification of... The additive approach to compatibilization is limited by the fact that there is a lack of economically viable routes for the synthesis of suitable block and graft copolymers for each system of interest. The compatihilizer market is often too specific and too small to justify a special synthetic effort. [Pg.415] Moreover, commercially available triblock copolymers designed to be thermoplastic elastomers, not compatihilizers, are often used in Heu of the more appealing diblock materials. Since the mid-1980s, the generation of block or graft copolymers in situ during blend preparation (158,168—176), called reactive compatibilization, has emerged as an alternative approach and has received considerable commercial attention. [Pg.415] Etherification and esterification of hydroxyl groups produce derivatives, some of which are produced commercially. Derivatives may also be obtained by graft polymerization wherein free radicals, initiated on the starch backbone by ceric ion or irradiation, react with monomers such as vinyl or acrylyl derivatives. A number of such copolymers have been prepared and evaluated in extmsion processing (49). A starch—acrylonitrile graft copolymer has been patented (50) which rapidly absorbs many hundred times its weight in water and has potential appHcations in disposable diapers and medical suppHes. [Pg.342] Copolymers of VDC can also be prepared by methods other than conventional free-radical polymerization. Copolymers have been formed by irradiation and with various organometaHic and coordination complex catalysts (28,44,50—53). Graft copolymers have also been described (54—58). [Pg.430] Although they lack commercial importance, many other poly(vinyl acetal)s have been synthesized. These include acetals made from vinyl acetate copolymerized with ethylene (43—46), propjiene (47), isobutjiene (47), acrylonitrile (48), acrolein (49), acrylates (50,47), aHyl ether (51), divinyl ether (52), maleates (53,54), vinyl chloride (55), diaHyl phthalate (56), and starch (graft copolymer) (47). [Pg.450] See other pages where Copolymers, graft is mentioned: [Pg.61] [Pg.111] [Pg.195] [Pg.452] [Pg.611] [Pg.251] [Pg.170] [Pg.174] [Pg.160] [Pg.245] [Pg.260] [Pg.459] [Pg.145] [Pg.268] [Pg.268] [Pg.268] [Pg.268] [Pg.268] [Pg.272] [Pg.15] [Pg.135] [Pg.364] [Pg.415] [Pg.415] [Pg.415] [Pg.416] [Pg.420] [Pg.87] [Pg.520] [Pg.520] [Pg.522] See also in source #XX -- [Pg.3 , Pg.10] See also in source #XX -- [Pg.39] See also in source #XX -- [Pg.260] See also in source #XX -- [Pg.176] See also in source #XX -- [Pg.77] See also in source #XX -- [Pg.3 , Pg.10] See also in source #XX -- [Pg.83] See also in source #XX -- [Pg.256] See also in source #XX -- [Pg.104] See also in source #XX -- [Pg.79 , Pg.93] See also in source #XX -- [Pg.187 , Pg.200] See also in source #XX -- [Pg.160] See also in source #XX -- [Pg.73] See also in source #XX -- [Pg.238 , Pg.294 , Pg.308] See also in source #XX -- [Pg.3 , Pg.10] See also in source #XX -- [Pg.64 , Pg.87] See also in source #XX -- [Pg.240] See also in source #XX -- [Pg.154] See also in source #XX -- [Pg.101] See also in source #XX -- [Pg.56] See also in source #XX -- [Pg.14 , Pg.14 , Pg.23 , Pg.111 , Pg.259] See also in source #XX -- [Pg.124] See also in source #XX -- [Pg.6 , Pg.28 , Pg.41 , Pg.43 , Pg.44] See also in source #XX -- [Pg.348 , Pg.349 , Pg.350] See also in source #XX -- [Pg.39] See also in source #XX -- [Pg.161] See also in source #XX -- [Pg.208 , Pg.299 , Pg.321] See also in source #XX -- [Pg.659] See also in source #XX -- [Pg.230 , Pg.308] See also in source #XX -- [Pg.226] See also in source #XX -- [Pg.602] See also in source #XX -- [Pg.29 , Pg.358 , Pg.359] See also in source #XX -- [Pg.1036] See also in source #XX -- [Pg.94 , Pg.161] See also in source #XX -- [Pg.220] See also in source #XX -- [Pg.52] See also in source #XX -- [Pg.580] See also in source #XX -- [Pg.588] See also in source #XX -- [Pg.319 , Pg.320 , Pg.332] See also in source #XX -- [Pg.287] See also in source #XX -- [Pg.1036] See also in source #XX -- [Pg.46] See also in source #XX -- [Pg.4] See also in source #XX -- [Pg.285] See also in source #XX -- [Pg.112] See also in source #XX -- [Pg.3 , Pg.172 , Pg.190] See also in source #XX -- [Pg.326 , Pg.327] See also in source #XX -- [Pg.24] See also in source #XX -- [Pg.34 , Pg.159] See also in source #XX -- [Pg.22] See also in source #XX -- [Pg.329 , Pg.330 , Pg.331 , Pg.335 , Pg.336 , Pg.338] See also in source #XX -- [Pg.111 , Pg.115 , Pg.930 , Pg.935] See also in source #XX -- [Pg.374 , Pg.377 , Pg.378 , Pg.379 , Pg.380 , Pg.381 , Pg.382 , Pg.383] See also in source #XX -- [Pg.112] See also in source #XX -- [Pg.252 , Pg.253 , Pg.254 , Pg.255 , Pg.256] See also in source #XX -- [Pg.8] See also in source #XX -- [Pg.27] See also in source #XX -- [Pg.8 , Pg.9 , Pg.11 , Pg.11] See also in source #XX -- [Pg.81] See also in source #XX -- [Pg.3] See also in source #XX -- [Pg.102 , Pg.137 , Pg.201 , Pg.409] See also in source #XX -- [Pg.157] See also in source #XX -- [Pg.424] See also in 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Applications of graft copolymers Biopolymer-based stimuli-sensitive functionalized graft copolymers Blend grafted copolymer Blends, grafts and copolymers Block and Graft Copolymers by Successive Addition Block and graft copolymer micelles in aqueous medium Block and graft copolymers Block/graft copolymers Butadiene copolymer grafted with Cationic graft copolymer Monomer Cationic graft copolymer Polymerization Cationic graft copolymers Cationic starches graft copolymers Cellulose acetate graft copolymer Cellulose copolymers, graft copolymerization Cellulose graft copolymers Cellulose graft copolymers Synthesis Cellulose graft copolymers chemical modifications Cellulose graft copolymers selection Cellulose-polystyrene graft copolymer Cellulose-starch graft copolymers Chitosan/poly graft copolymers Click graft copolymers Coating, graft copolymers Collagen graft copolymer Comb and graft copolymers Comb graft copolymer Compatibilization by graft copolymer formation Compatibilization with graft copolymers Composites Graft copolymers Copolymer , graft curve Copolymer , graft diagram Copolymer , graft ideal Copolymer , graft living Copolymer , graft multicomponent Copolymer formation, graft Copolymer radiation grafting advantages Copolymer synthesis, graft groups Copolymer, graft random Copolymerisation graft copolymers Copolymerization graft copolymers Copolymers hydrophilic-hydrophobic grafts Copolymers with long grafts Copolymers with short grafts Copolymers, amphiphilic grafted Copolymers, graft amphiphilic type Copolymers, graft anionic polymerization methods Copolymers, graft cellulosic type Copolymers, graft comb-type synthesis Copolymers, graft emulsifying properties Copolymers, graft ether copolymerization Copolymers, graft macromonomer synthesis method Copolymers, graft methacrylates Copolymers, graft model polymerization methods Copolymers, graft radical polymerization methods Copolymers, graft synthesis procedure Copolymers, graft water absorbing properties Copolymers, hydrophobic hydrophilic polymer grafted Copolymes, graft Copolymes, graft characterization Copolymes, graft properties Crosslinked graft copolymers Dextran-grafted acrylamide copolymer Dextran-methyl methacrylate graft copolymers Diblock copolymer grafted particles Dispersing agent graft copolymers Double hydrophilic graft copolymers Drug graft copolymers EPR graft copolymers Emulsion polymerization graft copolymers Epoxy acrylic copolymer graft composition Epoxy acrylic copolymer grafting mechanism Epoxy acrylic graft copolymer Ethylene vinyl acetate copolymers, graft Exact graft copolymer Experimental Details About Hyperbranched Graft Copolymers Formaldehyde graft copolymer Formation of Graft Copolymers Functional grafting, styrenic copolymers Gradient-graft copolymers Graft Copolymers as Reinforcing Agents in Green Composites Graft Copolymers of Polysaccharides Graft acetate copolymers Graft copolymer Biodegrade Graft copolymer Experimental conditions Graft copolymer Synthesis data Graft copolymer Terms Links Graft copolymer alloys, impact strength Graft copolymer amidation Graft copolymer aminolysis Graft copolymer applications Graft copolymer butyl acrylate/methyl methacrylate Graft copolymer compositions Graft copolymer density Graft copolymer products Graft copolymer solution properties Graft copolymer stabilization Graft copolymer stabilization aqueous suspensions Graft copolymer structures Graft copolymer styrene-poly Graft copolymer synthesis advantages Graft copolymer synthesis copolymerization Graft copolymer synthesis grafting from - surface initiated Graft copolymer synthesis grafting from polymer surfaces Graft copolymer synthesis grafting through - copolymerization Graft copolymer synthesis mechanisms Graft copolymer synthesis polymer transfer Graft copolymer synthesis polymerization Graft copolymer synthesis redox polymerization Graft copolymer synthesis with living radical polymerization Graft copolymer synthesis with transformation reactions Graft copolymer thermoplastic elastomers, structure Graft copolymer, definition Graft copolymer, definition preparation Graft copolymer, properties Graft copolymers Anticorrosive Graft copolymers acid)/methyl methacrylate Graft copolymers acrylate Graft copolymers alternative names Graft copolymers biodegradability Graft copolymers characterization Graft copolymers controlled initiation, scheme Graft copolymers dendron Graft copolymers derivatives Graft copolymers dynamic mechanical analysis Graft copolymers effects Graft copolymers ether) Graft copolymers free radical initiator concentration Graft copolymers from anionic Graft copolymers from anionic polymerization Graft copolymers general Graft copolymers glycol)/styrene Graft copolymers grafting from Graft copolymers grafting method Graft copolymers grafting onto Graft copolymers grafting through Graft copolymers highest yields Graft copolymers initiation methods Graft copolymers macromolecular engineering Graft copolymers mechanical forces, synthesis Graft copolymers mercaptans Graft copolymers methacrylate Graft copolymers methacrylate)/styrene Graft copolymers molecular weight characteristics Graft copolymers novel Graft copolymers of cellulose Graft copolymers particle size distribution Graft copolymers phase separation Graft copolymers poly /methyl methacrylate Graft copolymers poly 1/methyl acrylate Graft copolymers poly ethyl Graft copolymers polymerizations Graft copolymers polymers Graft copolymers polyol polyethers Graft copolymers preparation Graft copolymers preparation, active chloride Graft copolymers reinforced thermoplastic Graft copolymers solubility data Graft copolymers sulfonation Graft copolymers technique Graft copolymers tensile strength Graft copolymers water sorption Graft copolymers with acid-sensitive Graft copolymers with the aid of macromonomers Graft copolymers, morphology Graft copolymers, polymeric surfactants Graft copolymers, polymeric surfactants suspension stabilization Graft copolymers, polymeric surfactants synthesis Graft copolymers, polyolefin Graft copolymers, synthesis Graft copolymers, wettability Graft copolymers, with cellulose Graft copolymers. See Graft polymer and copolymer Grafted Block Copolymers Grafted block copolymer networks formed Grafted copolymers Grafted copolymers Grafted onto polybutadiene copolymer Grafting copolymers Grafting copolymers Grafting copolymers, importance Grafting graft copolymers Grafting purification, graft copolymer Grafting-through approach copolymers Group transfer polymerization graft copolymers High impact polystyrene (HIPS graft copolymer Hybrid graft copolymers Hybrid graft copolymers using Hydrolyzed graft copolymers In situ graft copolymer Isoprene graft copolymers Lignin cationic graft copolymer Lignin graft copolymers Lignin-polystyrene graft copolymers Living radical polymerization graft copolymer synthesis Macroinitiators graft copolymers Macromonomers graft copolymers Maleic acid-starch graft copolymers Methacrylic acid graft copolymers Methacrylonitrile-starch graft copolymers Methyl methacrylate copolymer grafted onto polybutadiene Methyl methacrylate-starch graft copolymers Microwave-irradiated synthesis, agar-based graft copolymers Microwave-irradiated synthesis, agar-based grafted copolymers Molecular weight distribution graft copolymers Morphology of graft copolymers Multiphase polymers graft copolymers Nanoparticles graft copolymers Natural rubber graft copolymers Nomenclature graft copolymers Nylon Graft Copolymers Other Approaches to Graft Copolymers PE graft copolymers PEMs graft copolymer PEO Block and Graft Copolymers PVA graft copolymer Partially fluorinated graft copolymer Phase separation block/graft copolymers Photochemical syntheses of graft-copolymers Poly -starch graft copolymers Poly -styrene radiation graft copolymer Poly -vinyl graft copolymers Poly derivative graft copolymer Poly graft copolymer Poly graft copolymers, anionic polymerization Poly polyamine graft copolymer Polyacrylamide-starch graft copolymers Polyacrylonitrile-starch graft copolymers Polyamide Graft Copolymers Polyamine-graft copolymers Polyaniline graft copolymers Polycaprolactone graft copolymers Polydimethylsiloxane) copolymer graft Polyethylene glycol grafting polymers/copolymers Polyethylene graft copolymers Polylactide graft copolymers Polymer blends graft copolymers Polymethylmethacrylate-methacrylic methacrylate, graft copolymer Polyolefine polyamide graft copolymers Polyoxyethylene, graft copolymer Polypyrrole graft copolymer, self-dope Polypyrroles graft copolymers Polysaccharide Graft Copolymers - Synthesis, Properties and Applications Polysaccharides graft copolymers Polystyrene graft copolymers Polystyrene graft copolymers, anionic Polythiophene-polystyrene graft copolymers Polythiophenes graft copolymers Polyurethane-grafted copolymer Polyvinyl/polypeptide graft copolymers Preparation of Hyperbranched Graft Copolymers Properties of Polysaccharide Graft Copolymers Proton exchange membrane graft copolymer Pyrrole/styrene graft copolymers Random and graft copolymers Saponified graft copolymers Siloxane Containing Graft and Segmented Copolymers by Free-Radical Copolymerization Solution-Type Graft Copolymers Stability starch graft copolymers Starch derivatives graft copolymers Starch graft copolymers Starch-polyester Graft Copolymer Styrene, graft copolymers with Styrene, graft copolymers with acrylate) Styrene, graft copolymers with methacrylate) Styrene, graft copolymers with poly Styrene, graft copolymers with poly ethyl Styrene-acrylonitrile copolymer grafting Styrene-butadiene rubber copolymer grafting Styrene-polypropylene graft copolymers Styrene-starch graft copolymers Styrene-starch graft copolymers production Styrene/methyl methacrylate copolymer grafted onto Superabsorbent graft copolymers Supramolecular graft copolymers Surface Graft Copolymers Surface active graft copolymers Surface-grafted copolymers Survey of Graft Copolymer Synthesis Synthesis of Graft Copolymers Tailored graft copolymers Testing graft copolymers Thermoplasticity graft copolymers Thermoresponsive materials graft copolymers with Transmission graft copolymer Use of graft copolymers Vinyl acetate copolymers, graft polymerization Vinyl acetate graft copolymers Vinyl acetate-starch graft copolymers Vinyl chloride graft copolymers Water-soluble lignin graft copolymers Fact Checked Content Last Updated: 27.08.2024 9 min reading time Content creation process designed by Content cross-checked by Content quality checked by Save Article Save Article Graft copolymers are an important and versatile class of copolymers. They are characterized by one or more polymer chains that are grafted onto the backbone of a different polymer. This unique structure gives graft copolymers distinctive physical and chemical properties, making them useful in a variety of applications like adhesives, coatings, and medical devices.In graft copolymers, the backbone represents the main polymer chain. The side chains are additional polymer branches grafted onto this backbone. This configuration is like the trunk of a tree with branches extending out. The synthesis methods, length of the side chains, and the number of grafting points play crucial roles in dictating the properties of the copolymer.The ability to fine-tune the properties of graft copolymers has led to them being termed 'designer polymers'. By adjusting variables such as the degree of polymerization or the type of monomers used, you can create materials with specific characteristics tailored to particular end-uses.Studying graft copolymers often involves understanding their molar mass distribution and grafting density. For instance, the molar mass (\(M_n\)) of a graft copolymer can be represented as a weighted combination of the backbone and side chains:\[M_n = M_{backbone} + \frac{n_g \times M_{side}}{n_g + 1}\]Where:\(M_{backbone}\): Molar mass of the backbone.\(M_{side}\): Molar mass of side chains.\(n_g\): Number of grafting sites. Let's consider a graft copolymer consisting of a polystyrene backbone with poly(methyl methacrylate) side chains. If the backbone's molar mass is 100,000 Da and the side chains have a molar mass of 10,000 Da with 20 grafting sites, calculate the molar mass of the graft copolymer.Given:\(M_{backbone} = 100,000 \text{ Da}\)\(M_{side} = 10,000 \text{ Da}\)\(n_g = 20\)Using the formula:\[M_n = 100,000 + \frac{20 \times 10,000}{21}\]\[M_n = 100,000 + 9,523.81 = 109,523.81 \text{ Da}\]Hence, the molar mass of the graft copolymer is approximately 109,524 Da. Graft copolymers are often used to improve the compatibility of different polymers in blended materials, enhancing their mechanical properties.Graft copolymers are created using various synthesis methods, each of which imparts unique characteristics to the final product. These methods generally involve the formation of a main polymer chain (the backbone) followed by the attachment of side chains. This section will introduce you to the most common techniques used in their synthesis.The grafting onto method involves preformed polymers that are chemically linked to a backbone polymer. The process can be challenged by steric hindrance, limiting the number of side chains that can attach. However, this technique allows for precise control over the nature and length of the side chains.Grafting onto is often used when the desired functionality is not achievable through other methods. This technique can facilitate the attachment of functional groups that are sensitive to the conditions used in other synthesis methods, thus preserving the structural integrity of the grafted polymers.In the grafting from method, the initiator is attached to the backbone, and polymerization occurs, growing the side chains directly from the backbone itself. This method usually leads to high grafting densities and offers better control over the polymer architecture.The grafting from method is favored in industrial applications due to its suitability for large-scale production.The grafting through method involves the copolymerization of macromonomers with other monomers to form graft copolymers. This method is advantageous for the formation of well-defined structures and uniform graft distributions. To illustrate the grafting through method, consider the copolymerization of a polystyrene macromonomer with ethylene monomers. The resulting graft copolymer features polystyrene side chains integrated within a polyethylene backbone, achieving a combination of properties from both polymers. MethodAdvantagesDisadvantagesGrafting OntoPrecision in chain length and compositionLimited graft densityGrafting FromHigh graft density, suitable for large scaleComplex initiation processGrafting ThroughWell-defined structure, uniform distributionLimited to suitable macromonomersBy understanding these methods, you can choose the appropriate synthesis approach according to the desired properties and application of the graft copolymer.Understanding the mechanism of graft copolymerization is crucial for manipulating the structure and properties of these polymers for various applications. The process can involve several mechanisms based on the method selected for polymerization. Let's dive into some of these mechanisms to see how they influence the characteristics of graft copolymers.In free radical graft copolymerization, free radicals are generated on the backbone polymer, initiating the polymerization of grafted side chains. The general steps include initiation, propagation, and termination, similar to conventional free radical polymerization. However, here the free radicals initiate at specific points on the polymer backbone.Oxygen, heat, or light can typically initiate the formation of free radicals in the polymer backbone, making this method very versatile.Free radical graft copolymerization can lead to a more complex molecular architecture due to the random nature of free radical generation. This can sometimes result in uneven grafting, but it can also be beneficial for creating polymers with unique properties like thermoplastic elastomers, where flexibility and toughness are combined.Another important mechanism is ionic graft copolymerization, which involves cationic or anionic initiators that create charged sites on the polymer backbone. This process provides high control over molecular weight distribution and results in more uniform grafting compared to free radical methods. Consider using lithium initiators to create carbanions on a polymer backbone like polybutadiene. The side chains can then be polymerized from these anionic sites, resulting in highly controlled graft copolymers. In coordination graft copolymerization, catalyst complexes are used to initiate polymerization at specific sites on the backbone. This technique is often used for adding polyethylene or polypropylene branches to a different polymer backbone, allowing for the combination of properties from various polymer families. Let's take a scenario where zirconocene catalysts are used in coordination graft copolymerization. These catalysts attach to polymer backbones to precisely grow side chains of polyolefins, enabling the combination of features such as toughness and processability in a single copolymer. MethodInitiators/CatalystsAdvantagesFree RadicalOxygen, heat, lightVersatile and easy to performIonicLithium, boron compoundsControl over molecular weightCoordinationZirconocene, titaniumCombines diverse polymer propertiesBy selecting the appropriate mechanism, you can tailor the resulting copolymer's structure and characteristics, aligning them with specific industrial or commercial needs.Graft copolymers are valuable due to their ability to combine multiple properties, thereby enhancing material performance in specific applications. Their unique structure, where branches of different polymers are grafted onto a main polymer backbone, allows for tailored functionality and versatility. This potential makes them notably useful in fields such as biomedical engineering, adhesives, and coatings.In the realm of biomedical engineering, graft copolymers bring innovative solutions due to their biocompatibility and functional versatility. They can be customized to meet the demanding requirements of medical applications, such as drug delivery systems, tissue engineering, and implants.One of the primary uses of graft copolymers in this field is in creating hydrogels. These water-swollen polymer matrices can be engineered to respond to various stimuli, such as pH or temperature, making them ideal for controlled drug release applications. Hydrogels: Networks of polymer chains that contain a large amount of water, often used in drug delivery and tissue engineering due to their biocompatibility. An example of graft copolymers in use is poly(N-isopropylacrylamide)-g-polyethylene glycol (PNIPAAm-g-PEG). This copolymer is used to create temperature-sensitive hydrogels that shrink or swell in response to body temperature, thus delivering drugs in a controlled fashion. Graft copolymers' application extends to tissue scaffolding, where they serve as frameworks allowing cell attachment and growth. By mimicking the natural extracellular matrix, these scaffolds can support new tissue formation. Innovations are focusing on bioactive graft copolymers that can release growth factors to promote healing and regeneration. This capability is under significant research to advance regenerative medicine practices.The flexibility of graft copolymers in biomedical applications also lends itself to improve the compatibility of medical devices with body tissues, reducing the risk of immune rejection. Graft copolymers are copolymers with polymer chains grafted onto a different polymer backbone, offering unique physical and chemical properties.Synthesis involves creating a main polymer chain (backbone) with side chains attached, using methods like grafting onto, from, and through.Grafting mechanisms include free radical, ionic, and coordination, affecting polymer structure and properties.Graft copolymers can enhance compatibility in polymer blends, useful in applications such as adhesives, coatings, and biomedical fields.An example includes PNIPAAm-g-PEG used in hydrogels for controlled drug delivery, responsive to stimuli like temperature.In biomedical engineering, graft copolymers are employed for drug delivery systems, tissue engineering, and improving biocompatibility of medical devices. What are the applications of graft copolymers in biomedical engineering? Graft copolymers are used in biomedical engineering for drug delivery, tissue engineering, and as scaffolds for cell growth due to their enhanced biocompatibility and tunable properties. They can also be utilized in developing sensors, hydrogel-based wound dressings, and as carriers for controlled release of therapeutic agents. How are graft copolymers synthesized? Graft copolymers are synthesized through methods such as "grafting onto," "grafting from," and "grafting through," which involve initiating polymerization on a preformed backbone to attach side chains, either by chemical reactions at reactive sites or by using radical, ionic, or other polymerization techniques. What are the advantages of using graft copolymers in material science? Graft copolymers offer enhanced material properties by combining the attributes of different polymers, such as improved mechanical strength, thermal stability, and chemical resistance. They enable targeted functionality and compatibility in complex systems, facilitating advancements in tailored materials for specific applications across industries. What are the properties of graft copolymers that make them suitable for industrial applications? Graft copolymers have a unique combination of properties from different monomers, offering enhanced chemical resistance, mechanical strength, and flexibility. They also exhibit improved adhesion, compatibility with diverse materials, and tailored thermal properties, making them versatile for coatings, adhesives, and other industrial applications. What are the main challenges in the production of graft copolymers? The main challenges in the production of graft copolymers include controlling the grafting density and distribution, achieving desired properties and compatibility between different polymer segments and substrates, ensuring uniformity and reproducibility, and optimizing reaction conditions to prevent side reactions and degradation. Once again we will only discuss a few of many graft copolymers that have been, or could be prepared by applying ATRP to materials synthesis. An early review on the preparation of graft copolymers by ATRP utilizing both "grafting through" and "grafting from" provided examples of poly(N-vinlpyrrolidone-g-styrene); poly(methyl methacrylate-g-dimethylsiloxane), discussed in greater detail below; poly(methyl methacrylate-g-lactide); poly(n-butyl acrylate-g-methyl methacrylate); and poly(n-butyl acrylate-g-ethylene) prepared by grafting through, and examples prepared by grafting from functionalized poly(isobutene), polyethylene, poly(vinyl chloride), poly(vinylidene fluoride).(1,2) With the development of various "click" chemistry reactions graft copolymers have also been prepared by "grafting to". Grafting through: In a "grafting through" copolymerization the reactivity ratio of monomers and macromonomers may be affected by micro-inhomogeneity of the reaction mixture in addition to the reaction mechanism. This has often been observed in macromonomer copolymerization, or "grafting through" copolymerization for preparation of graft copolymers that would be expected to undergo phase separation. For example, when MMA was copolymerized with a poly(dimethylsiloxane)-methacrylate macromonomer, the composition of the product was strongly affected by the reaction conditions.(3) As shown in the following cartoons, copolymerization by conventional FRP led to the preparation of copolymers that displayed a broad distribution of chain length and composition due to the continuous change in the instantaneous feed ratios of the comonomers remaining in the reaction medium and the effect of continuous initiation/growth/termination of the copolymerization throughout the reaction. At the other extreme ATRP performed in 30% xylene solution at 90 0C utilizing a compatible macroinitiator resulted in preparation of a uniform comb-like graft copolymer due to similar reactivity of both comonomers, (r ~1) in the diluted reaction solution. However, conducting ATRP or RAFT in only 3% xylene generated gradient copolymers, due to monomer feed variation throughout the reaction because of the impact of viscosity on macromonomer reactivity resulting in a higher reactivity ratio for MMA, (r~2), compared to the macromonomer. The following schematics illustrate the differences in the microstructure and also the dramatic affect the differences in microstructure had on tensile properties. The tapered, or gradient graft copolymer has a tensile elongation of only ~30%, compared to ~120% for the irregular non-homogeneous product formed by FRP, or the~280% for a regular comb copolymer.(4) These dramatic differences in physical properties occur even though all three copolymers have approximately the same overall composition (~50/50) and the same overall molecular weight Mw~100,000. Topological control can also be extended to heterograft copolymers(5) where graft copolymers with grafts of different composition can be prepared in a one step or two step CRP grafting through procedure with two different macromonomers forming copolymers with different gradient distributions of grafts along the backbone of the copolymer. In the following set of schematics the different reactivity of a PLA macromonomer and a PDMS macromonomer are shown to result in the preparation of a gradient copolymer with a gradient of both macromonomers along the polymer backbone. The PLA-M is preferentially incorporated while the PDMS-M is incorporated later in the copolymerization process forming a copolymer with a higher concentration of PLA grafts at one chain end and a higher concentration of PDMS grafts at the other. This situation is amplified when a two step copolymerization is conducted. ATRP of two poly(ethylene oxide) (PEO) macromonomers, with different degrees of polymerization (DPn) and different end groups, was conducted in solution via the grafting through method.(6) Selection of a PEO methacrylate with a methyl end-group (PEOMeMA, DPPEO = 23) and a PEO acrylate end-capped by a Phenyl ring (PEOPhA, DPPEO = 4) for the copolymerization led to a spontaneous gradient of PEO grafts along the copolymer backbone. A spontaneous gradient copolymer was formed because of significantly different reactivity of the two PEO macromonomers. The resulting copolymer has PEOMeMA at one end of the polymer chain, gradually changing through hetero-sequences to predominately PEOPhA grafts at the other chain end. An increase in the initial feed ratio of PEO acrylate reduced the rate of change in the shape of the gradient. Amorphous-crystalline structure in the copolymers was demonstrated by DSC and WAXS. The mechanical measurements of copolymers consisting of an amorphous PEOPhA and crystallizable PEOMeMA segments indicated elastomeric properties in the range of a soft rubber (G' approximately 104 Pa, G' >> G''). Grafting from: Graft copolymer with a poly(vinyl chloride) backbone were prepared by two approaches, one was preparation of a macroinitiator by copolymerization of vinyl chloride with a monomer containing an ATRP initiating group, vinyl chloroacetate.(7) The other was to graft from inherent structural defects in poly(vinyl chloride.(8) Either approach can be considered to be a viable approach to self plasticized PVC.(9) Another example of a graft copolymer prepared by ATRP using the "grafting from" approach is the formation of a polyethylene-g-poly(n-butyl acrylate) copolymer which used a polyethylene macroinitiator with distributed α-bromoisobutyrate functionality. The copolymers were prepared using a less active BA6TREN based ligand that was soluble in the reaction medium to controllably polymerize butyl acrylate in a solution of the polyethylene macroinitiator.(10,11) Depending on the mole ratio of the segments such a material could find application as an impact modifier for polyethylene, a compatibilizer in polyethylene blends, as a surfactant or as a surface modifier to provide better adhesive properties. The macroinitiator was prepared by copolymerization of ethylene with undecenol using a zirconocene based catalyst. The pendant hydroxyl groups were esterified ml 2-bromopropionyl bromide for a butyl acrylate grafting from reaction. There is strong incompatibility between the components and the final copolymer, containing 32-67% butyl acrylate units, showed both clear melting and crystallization peaks attributable to polyethylene and a glass transition from the poly(butyl acrylate). At lower mole fractions of poly(butyl acrylate) the matrix was based on polyethylene and displayed good extensibility as well as molecular and structural orientability while the material with a poly(butyl acrylate) matrix displayed a loss of resistance to tensile deformation. Below the glass transition the of the PBA phase the PBA seems to play a role of reinforcement in the PE matrix, so that the modulus of the material can even exceed the values determined for the pure polyethylene. Above the glass transition of the PBA, the soft phase of grafts influences the modulus of the polymers to a degree dependent on composition. A strong effect of the presence of the grafted chains was also seen in the molten state in which the grafted polymers behave as elastomers with remarkably higher modulus than that determined for the entangled polyethylene. The observed behavior should be related to the two phase structure of the system with PBA micro-domains dispersed in the PE matrix and networked by the PE backbone chains. As shown below the PE-g-MMA demonstrate good performance as a compatibilizer between the two homopolymers when the blends were studied by TEM.(12) Grafting to: As discussed on page 7 graft copolymers can also be prepared by "grafting to" reactions.(13-15) While grafting to is perhaps the oldest procedure for preparation of graft copolymers in free radical chemistry, e.g., impact resistant polystyrene, properties of materials prepared by grafting to in a controlled polymerization process has not yet gained a significant amount of attention. REFERENCES (1) Boerner, H. G.; Matyjaszewski, K. Macromol. Symp. 2002, 177, 1. (2) Inceoglu, S.; Olugebefola, S. C.; Acar, M. H.; Mayes, A. M. Designed Monomers and Polymers 2004, 7, 181-189. (3) Shinoda, H.; Miller, P. J.; Matyjaszewski, K. Macromolecules 2001, 34, 3186-3194. 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