

[0434] The concentration of the solute in a reaction solution is 5% by mass to 70% by mass, and preferably 10% by mass to 50% by mass. The reaction temperature is usually 10° C. to 150° C., preferably 30° C. to 120° C., and more preferably 40° C. to 100° C.

[0435] The reaction time is usually 1 hour to 48 hours, preferably 1 hour to 24 hours, and more preferably 1 hour to 12 hours.

[0436] After completion of the reaction, the reaction solution is allowed to be cooled to room temperature and purified. The purification may be performed by normal methods, and these methods can be applied to the invention. For example, a liquid-liquid extraction method of applying water washing or combining it with an appropriate solvent to remove the residual monomers or oligomer components; a purification method in a solution state, such as ultrafiltration of extracting and removing only the polymers having a molecular weight not more than a specific value; a reprecipitation method of dropwise adding the reaction solution into a poor solvent to solidify the resin in the poor solvent, to thereby remove the residual monomers and the like; and a purification method in a solid state, such as washing of the slurry with a poor solvent after separation of the slurry by filtration. For example, the resin is precipitated as a solid by contacting the reaction solution with a solvent in which the resin is sparingly soluble or insoluble (poor solvent) in a volumetric amount of 10 times or less, preferably from 10 to 5 times, the reaction solution.

[0437] The solvent used at the operation of precipitation or reprecipitation from the polymer solution (precipitation or reprecipitation solvent) may be sufficient if it is a poor solvent for the polymer, and the solvent which can be used may be appropriately selected from a hydrocarbon, a halogenated hydrocarbon, a nitro compound, an ether, a ketone, an ester, a carbonate, an alcohol, a carboxylic acid, water, and a mixed solvent containing these solvents, according to the kind of the polymer. Of these solvents, a solvent containing at least an alcohol (especially, methanol or the like) or water is preferred as the precipitation or reprecipitation solvent.

[0438] The amount of the precipitation or reprecipitation solvent used may be properly selected considering the efficiency, yield and the like, but the amount used is generally 100 to 10,000 parts by mass per 100 parts by mass of the polymer solution, preferably 200 to 2,000 parts by mass, and more preferably from 300 to 1,000 parts by mass.

[0439] The temperature in precipitation or reprecipitation may be arbitrarily selected considering the efficiency or operability, but is generally on the order of 0° C. to 50° C., preferably in the vicinity of room temperature (for example, approximately 20° C. to 35° C.). The precipitation or reprecipitation operation may be performed using commonly employed mixing vessel such as stirring tank by a known method such as a batch system and a continuous system.

[0440] The precipitated or reprecipitated polymer is usually subjected to commonly employed solid-liquid separation such as filtration and centrifugation, then dried and used. The filtration is performed using a solvent resisting filter element preferably under pressure. The drying is performed under atmospheric pressure or reduced pressure (preferably under reduced pressure) at a temperature of approximately 30° C. to 100° C., and preferably on the order of 30° C. to 50° C.

[0441] Incidentally, after the resin is once precipitated and separated, the resin may be again dissolved in a solvent and then brought into contact with a solvent in which the resin is

sparingly soluble or insoluble. That is, there may be used a method comprising, after the completion of radical polymerization reaction, bringing the polymer into contact with a solvent in which the resin is sparingly soluble or insoluble, to precipitate a resin (step a), separating the resin from the solution (step b), anew dissolving the resin in a solvent to prepare resin solution A (step c), bringing the resin solution A into contact with a solvent in which the resin is sparingly soluble or insoluble in a volumetric amount of less than 10 times (preferably 5 times or less) the resin solution A, to precipitate a resin solid (step d), and separating the precipitated resin (step e).

[0442] The weight average molecular weight of the resin (P) for use in the invention is preferably 1,000 to 200,000, more preferably 2,000 to 50,000, and still more preferably 2,000 to 20,000.

[0443] The polydispersity (Mw/Mn) of the resin (P) is preferably 1.0 to 3.0, more preferably 1.0 to 2.5, and still more preferably 1.0 to 2.0. The weight average molecular weight and polydispersity of the resin (P) are defined in terms of polystyrene by the GPC method.

[0444] These resins (P) may be used as mixture of two or more kinds.

[0445] The addition amount of the resin (P) for use in the invention is preferably 30% by mass to 100% by mass, more preferably 50% by mass to 99.95% by mass, and especially preferably 70% by mass to 99.90% by mass, on the basis of all the solid contents of the composition. (In this specification, mass ratio is equal to weight ratio.)

[2] Hydrophobic Resin (HR)

[0446] Differently from the resin (P) as above, the actinic ray-sensitive or radiation-sensitive resin composition of the invention may contain a hydrophobic resin (HR). When exposure is performed by filling a liquid having a refractive index higher than that of air (e.g., pure water or the like) between a photosensitive film and a lens, that is, in the case of performing immersion exposure, or in the case of obtaining a negative pattern by using an organic developer as the developer, the hydrophobic resin (HR) is preferably used.

[0447] Since the hydrophobic resin (HR) is localized on the film surface, it is preferred to contain a group having a fluorine atom, a group having a silicon atom, or a hydrocarbon group having 5 or more carbon atoms. These groups may be contained in the main chain of the resin or may be substituted on the side chain.

[0448] The standard polystyrene equivalent weight average molecular weight of the hydrophobic resin (HR) is preferably 1,000 to 100,000, more preferably 1,000 to 50,000, and still more preferably 2,000 to 15,000.

[0449] Also, the hydrophobic resin (HR) may be used alone, or two or more kinds may be used in combination.

[0450] The content of the hydrophobic resin (HR) in the composition is preferably 0.01% by mass to 15% by mass, more preferably 0.05% by mass to 8% by mass, and still more preferably 0.1% by mass to 7% by mass, based on all the solid content in the composition of the invention.

[0451] Specific examples of the hydrophobic resins (HR) are shown below.