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PHYSICAL METHODS
OF INVESTIGATION

Redispersible Polymers Are Prepared in Supercritical Carbon Dioxide

S. Yu. Tuzova[a], **A. Yu. Nikolaev**[b], **L. N. Nikitin**[b],
A. A. Pestrikova[a], **and I. Yu. Gorbunova**[a]

[a] *Russian University of Chemical Technology, Moscow, Russia*
[b] *Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow, Russia*
e-mail: touzova@muctr.ru

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Abstract—A new method is proposed for preparing redispersible polymers in supercritical carbon dioxide; this method makes it possible to reduce the number of stages and simplify the hardware embodiment of the synthesis process.

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Currently, there is a steady trend towards the use as solvents for the synthesis of polymers in environmentally friendly inorganic media, including supercritical fluids, due to the ever rising requirements for the protection of the environment [1, 2].

EXPERIMENTAL

The setup used to prepare polymers comprised a manual piston pressure generator (90 mL working volume) for creating pressure of 50–400 atm. The system of valves provided the supply of CO_2 into reaction cells. The pressure generator and cells were equipped with pressure gages for rapid control over the pressure and a gas admission–release system. A thermostat was used to adjust and maintain the required constant temperature. Temperature regulation was performed with an accuracy of ±0.2°C. The cell was designed to conduct experiments at pressures of up to 1000 atm and temperatures of up to 300°C. A magnetic stirrer was placed inside the working cell. For preparing acrylate redispersible polymers, a 10-cm^3 stainless steel cell was charged with monomers and an initiator (azodiisobutyronitrile). The degree of cell fill was one-third. After pressurization and purging with compressed CO_2 gas, the cell was placed into a heating unit. After the time required for setting the desired temperature in the cell elapsed, the pressure required for the CO_2 in the system to acquire the supercritical state was adjusted by means of a manual pump.

After the synthesis of the polymer in supercritical carbon dioxide was over, heating was switched off and the pressure in the system was slowly released.

In order to prepare aqueous dispersions, redispersible polymers were dispersed into water by ordinary mechanical mixing at room temperature so as to obtain a stable 30% dispersion.

Thin polymer films based on aqueous polymer dispersions were cured at room temperature.

The IR spectra of polymers were recorded as KBr disks on an Nicolet FTIR-380 spectrometer having 2-cm^{-1} resolution in the range 400–4000 cm^{-1} at room temperature in the transmission mode.

The dynamic viscosity was measured as a function of shear stress on a Reotest-2 rotational viscometer. The principle of operation of this viscometer consists in the measurement of the lag angle α of the inner cylinder upon the deformation of the material placed in the gap between two coaxial cylinders at set test conditions (temperature and rotor speed).

THEORY

Supercritical fluids are a form of physical state of the matter to which many organic and inorganic compounds can go upon attainment of certain critical parameters (temperature and pressure); it is only necessary that the compound does not decompose at the critical temperature [3, 4].

After the critical point is achieved, the phase boundary between liquid and gas disappears and the compound acquires some physical properties having values intermediate between the properties of the liquid and gas. For example, a compound in the supercritical state acquires the density intrinsic to liquids and the high molecular mobility intrinsic to gases [5].

Water and carbon dioxides are among the supercritical inorganic fluids most widely used for the preparation of organic compounds. Meanwhile, the use of water, which has very high critical parameters (T_{cr} = 374.2°C, p_{cr} = 22.064 MPa) and is used primarily in decomposition and destruction processes, gives rise to a number of purely technological difficulties.

Carbon dioxide has relatively low critical parameters: $T_{cr} = 31°C$, $p_{cr} = 7.38$ MPa, and $\rho_{cr} = 0.468$ g/cm^3 (Fig. 1); it is nontoxic, non-flammable, non-explosive, cheap, and available. It is for this reason that supercritical carbon dioxide is widely used as the reaction medium, solvent, and catalyst of organic reactions and for the extraction of both vegetable and animal natural raw materials [6–12].

Polymer chemistry is one of the most promising application of supercritical CO_2 due to its ability to dissolve a wide range of organic compounds, which is a prerequisite for the synthesis of polymers [13].

The benefits from the method of preparing polymers where supercritical carbon dioxide is used as solvent are as follows: supercritical carbon dioxide has a high dissolving power and is inert to most monomers; it has a high diffusion coefficient (~100 times higher than in liquids) and a low viscosity (~10–100 times lower than in liquids); is easily removable without residue from the reaction zone on the completion of the synthesis and can be recycled; and it is non-toxic, inflammable, non-explosive, and environmentally safe; and cheap. Furthermore, there is no problem with chain termination and chain transfer to the solvent during polymerization.

Due to its high diffusion rates, supercritical carbon dioxide also makes it possible to easily carry out post-purification of the reaction product from residual monomers and initiator; it is sufficient to wash the resulting polymer with a fresh fluid. Such the obvious merits of supercritical carbon dioxide provide a wide range of its use in polymer chemistry. For example, supercritical CO_2 served to prepare polyimides [14–17], propylene oxide copolymers [18, 19], various polyacrylates [20], polyesters [21], 1-trifluoromethyl-1-ferrocenyl-2,2,2-trifluoroethyl methacrylate copolymers [22, 23], biodegradable polymers [24, 25], vinylpyrrolidone [26], ferrocene polyphenylenes [27, 28], polyaniline, [29] polyfluorenes [30, 31], polyphenylquinoxalines [32], polynaphthoylene benzimidazoles [33], and many other classes of polymers.

Those merits and the promise of supercritical carbon dioxide for use in polymer chemistry enabled us to develop a method for preparing redispersible polymers (which are a very popular type of polymeric materials) in this solvent.

Redispersible polymers are polymer powders which, can quickly form stable aqueous dispersions when dispersed in water, those dispersions being capable of forming a thin polymer films on the polymer surface. The chemical nature of these polymers should combine completely opposite properties, namely hydrophilicity and hydrophobicity. This allows both to provide a stable water-dispersed system and to counteract the washability after the formation of the coating. A neutral inorganic solvent (water) used in the preparation of dispersions based on redispersible polymers, makes it possible to prepare environmentally safe materials.

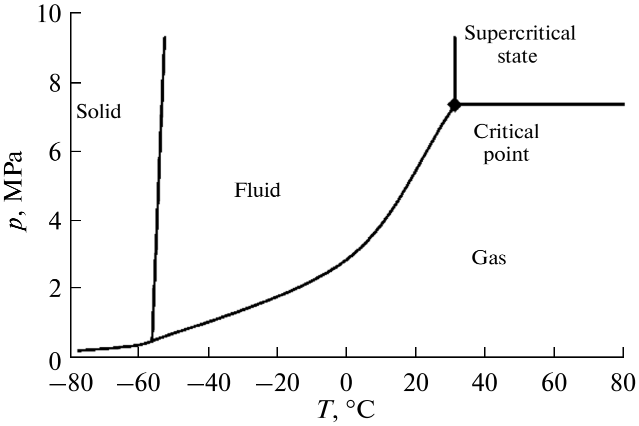

Fig. 1. Carbon dioxide phase diagram.

The application of redispersible polymer powders is very wide, ranging from design of their based paintwork materials to dry construction mixtures.

Redispersible polymers have a number of undoubted advantages over classic organic and aqueous solutions / dispersions of polymers, namely non-toxicity, fire and explosion safety, stability of the composition due to the nonoccurrence of sedimentation processes and chemical reactions during prolonged storage, and low costs of packaging, storage, and transport; storage and transportation of redispersible polymers are possible even in extremely difficult climatic conditions (from –40 to +40°C) without changing the characteristics of the redispersible polymer.

From the related literature [34–37], it flows that the preparation of this type of redispersible polymeric binder is carried out in an organic solvent or in water, followed by drying and grinding of the binder, which is accompanied by a plenty of waste.

Summing up the foregoing, we may state that the conventional technology of preparing redispersible polymers has the following drawbacks: large amounts of process waste (organic solvents and water) need to be recycled, and the hardware embodiment of the many-stage preparation process is complex.

One of the most promising ways to solve these problems, in our opinion, is to prepare redispersible polymers in supercritical fluids which can serve as a solvent in the process; this would appreciably simplify the preparation process, because major environmental problems arising from huge amounts of solvents that must be removed from the final product are thereby avoidable. Furthermore, when gaseous CO_2 is removed from the reaction zone by the end of the synthesis, the second technological problem is solved, namely, the final product can be easily and quickly purified from the remnant monomers by means of the CO_2.

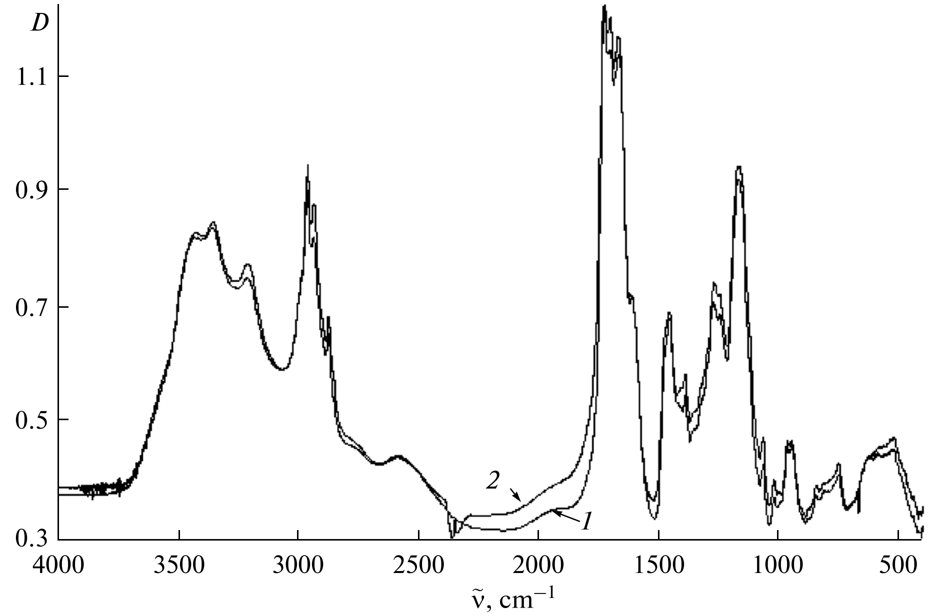

Fig. 2. IR spectra of redispersible acrylate polymers prepared (*1*) in aqueous media and (*2*) in supercritical carbon dioxide.

As can be inferred from the above, the merits of the proposed technology for preparing redispersible polymers in supercritical carbon dioxide are as follows:

—The process of preparing redispersible polymers is simplified due to the reduction of the number of process steps (there is no step of isolating the polymer from the solvent), because it is sufficient to merely remove the solvent from the redispersible polymer by the end of synthesis, because CO_2 will be independently removed from the reaction zone when going from the supercritical to normal state;

—The final product is prepared directly in powder, whose particle size can be regulated through preparation parameters (temperature and pressure);

—Liquid waste is absent;

—Carbon dioxide can be recycled; and

—Carbon dioxide, which is one of the most common by-products of many technological processes in various industries, is utilized.

RESULTS AND DISCUSSION

Redispersible materials can be prepared on the basis of diverse classes of polymers [38–42]. In our opinion, acrylic copolymers are most interesting in this regard due to their based coatings having such properties as high chemical resistance to corrosive media, resistance to ultraviolet radiation, good mechanical characteristics, low water adsorption, and low permeability for carbon dioxide.

We prepared redispersible acrylic copolymers according to the state-of-art method through emulsion polymerization in an aqueous medium, followed by separation of the polymer by spraying, and by our method, that is, in supercritical carbon dioxide.

The products produced by both methods were studied by IR spectroscopy. The identity of IR spectra implied that our prepared acrylate redispersible polymer had the same characteristics as the polymer prepared by the state-of-art method where the final product was isolated from the solvent by spraying (Fig. 2). From the identity of peaks that appeared in both spectra at 3400 cm^{-1} (ν(C=O)), 3150 cm^{-1} ($\nu_{as}(CH_2)$), 2950 cm^{-1} ($\nu_{as}(CH_3)$), 2580 cm^{-1} (ν(OH)), 1650–1750 cm^{-1} (ν(C=O)), 1450 cm^{-1} ($\delta(CH_2)$), 1300 cm^{-1} (ν_{as}(C–C–O), ν(C–O)), 1150 cm^{-1} (ν_s(C–C) and δ(CH)), we can infer that the two polymers have similar chemical structures.

It is thus proven that the preparation of an acrylate redispersible polymer in supercritical carbon dioxide offers an alternative to the state-of-art preparation method and can provide acrylic copolymers having a tailored set of characteristics.

It should be noted, however, that the redispersible polymers prepared by both methods had rather high molecular weights, and this inhibited the preparation of aqueous dispersions on their basis. In order to limit the increase in the copolymer molecular weight during synthesis both in supercritical carbon dioxide and in water, we added the reaction mass with *n*-dodecylmercaptan in an amount of 3% of the weight of reagents; those additions enabled us to appreciably reduce the molecular weight of the product and improve the redispersibility of the polymer.

Meanwhile, it is generally known that the stability of aqueous dispersions of polymers is in most cases due to the presence of small additives (emulsifying agents and dispersants) in their structure, and in similar dispersions from redispersible polymers, the stability is due to the presence of protective colloids in the dispersion [43–47].

Being guided by the above, we proposed a number of small additives and protective colloids that would be helpful to obtain stable aqueous dispersions based on redispersible polymers. We found that emulsifiers suitable for this purpose are those conventionally used for preparing water-dispersible polymers, such as anionic emulsifiers, exemplified by alkali metal alkyl sulfonates and alkyl phosphates, and some others. Of the protective colloids usually used to prepare redispersible polymers, the best choice is acetoacetic group modified poly(vinyl alcohol) with a degree of saponification between 92 and 98% and an average degree of polymerization between 350 and 450.

In order to facilitate the preparation of these materials, we proposed to introduce the above small additives and a protective colloid during the synthesis of polymers. Functional additives only insignificantly affected the run of the synthesis of acrylic redispersible ñîpolymers in supercritical carbon dioxide, but later provided an appreciable improvement of the redispersibility of the product and enhanced the production of a stable aqueous dispersion.

The redispersible polymers prepared in aqueous media or in supercritical carbon dioxide, were dispersed in water to yield aqueous dispersions that remained unbroken during 24 h and had similar structural parameters, as proven by the viscosity curves for aqueous dispersions of both polymers (Fig. 3).

Figure 3 implies that the logarithmic values of the lowest Newtonian viscosity for aqueous dispersions of both redispersible polymers are within 0.55–0.75. The logarithmic shear rate corresponding to the complete destruction, is in all cases not high and has a value of about 2.2–2.5. Thus, experimental data indicate moderate degrees of structuring in aqueous dispersions of redispersible polymers and their redispersibility under small shear forces.

Redispersible polymers prepared in water or in supercritical carbon dioxide served us to prepare redispersible dyes formulated as pigmented powder paintwork materials comprising an inorganic binder and a redispersible polymer powder with various additives whose formulations we developed earlier [47]. The coatings comprising those paintwork materials had similar and high performance characteristics. For example, both coatings had maximal adherence to glass and metals (5 points), elasticity of 1 mm, and impact strength of 14.7 J. Similar values of performance characteristics are indicative of the interchangeability of the two polymeric binders.

In summary, our proposed a method for preparing redispersible polymers in supercritical carbon dioxide is very promising and environmentally friendly. A water-redispersible polymer prepared in supercritical CO_2 is suitable for use both in preparing aqueous dispersions intended for providing thin protective films and in modifying inorganic binders for paintwork, civil construction, and other applications. Not only does this preparation method enhance the preparation technology, but it also provides the aforementioned polymers with a wide range of tailored performance characteristics dictated by the wide application range of water-redispersible polymers.

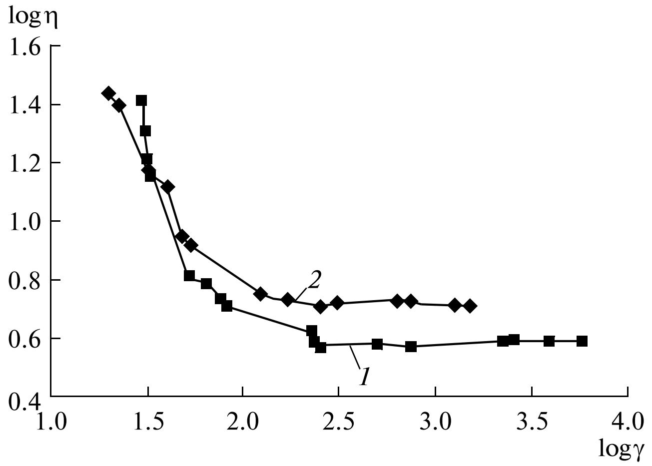

Fig. 3. Viscosity curves for aqueous dispersions of polymers prepared (*1*) in supercritical carbon dioxide and (*2*) using the state-of-art method in aqueous medium.

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