Education beyond traditional ages for schooling is an important source of human capital acquisition among adult women. Welfare reform, which began in the early 1990s and culminated in the passage of the Personal Responsibility and Work Opportunity Reconciliation Act in 1996, has promoted work rather than educational acquisition for this group. Exploiting variation in welfare reform across states and over time and using relevant comparison groups, we undertake a comprehensive study of the effects of welfare reform on adult women’s educational acquisition. We first estimate effects of welfare reform on high school drop-out of teenage girls, both to improve on past research on this issue and to explore compositional selection that may be relevant for our primary analyses of the effects of welfare reform on the educational acquisition of adult women. We conduct numerous specification checks and explore the mediating role of work. Based on a difference-in-difference-in-differences (DDD) framework, we find robust and convincing evidence that welfare reform significantly decreased the probability of college enrolment among adult women, by at least 20%. It also appears to have decreased the probability of high school enrolment on the same order of magnitude. These results suggest that the gains from welfare reform in terms of increases in employment and reductions in caseloads have come at a cost in terms of lower educational attainment among adult women at risk for relying on welfare. While not every potential welfare recipient would benefit from a high school or a college education, it cannot be assumed that the large negative aggregate effects of welfare reform on formal educational enrolment among adult women are an economically efficient or socially desirable outcome. Lower educational attainment may also have negative implications for these women’s health, as the literature has concluded in favor of a causal impact from higher education to better health. A comprehensive assessment of the costs and benefits of welfare reform would need to factor in these impacts.